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THEORY OF IGNITION OF SOLID PROPELLANTS

by

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ABSTRACT. Surface ignition of solid propellants has been represented by several analytical models, each involving obvious compromises with regard to scope of applicability. These models are distinguishable primarily in terms of site of the exothermic reaction governing ignition. Early research with nitrocellulose led to development of a theory involving chemical heat generation in the condensed phase. Two subsequent theoretical models were developed to explain ignition of the solid fuel ingredient of a composite propellant in an oxidizing atmosphere, and these two models were then extended on a heuristic basis to encompass a composite propellant in an inert atmosphere in which the oxidizing gas was produced by decomposition of the solid oxidizer. These two models are distinguished by whether the oxidation occurs at the surface or in the gas film above the surface.

This report reviews the solid, heterogeneous, and gas-phase ignition theories and reviews the nature and implications of the assumptions involved. It is concluded that, while possessing certain drastic simplifications in common, the various quantitative models differ so conspicuously in their assumptions regarding external initiating stimulus as to make quantitative comparisons or tests of validity impossible.



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FOREWORD

This report was prepared as part of a research program at the U. S. Naval Ordnance Test Station (NOTS) on the subject of Ignition of Solid Propellant Rockets, sponsored under RMMP-22-066/216-1/R001-06-01. The project assignment calls for conduct of research, and coordination of U. S. Bureau of Naval Weapons research projects in this field. One of the early efforts towards this combined objective was the preparation of a bibliography of relevant references to rocket ignition (NAVWEPS Report 8365, NOTS TP 3263). As work continued, it became evident that the existing competitive theories of propellant ignition were each inadequate, and that comparison and combination of the theories was impeded by lack of an objective, parallel presentation of the theories in a single source with consistent notation. This situation in turn impeded objective experimental evaluation of the theories, and thus prevented that progressive interplay of theory and experiment that normally is so essential for scientific progress. In an effort to resolve this impasse, a review of current theories was made, and was followed by a series of seminars to bring out the relative attributes and demerits of the theories. The outcome of this study was summarized in the present report. The reviews and description of the condensed phase, heterogeneous and gas-phase theories were carried out by H. H. Bradley, Jr., G. L. Dehority and M. M. Ibiricu, respectively. The introduction and summary were prepared by E. W. Price. Because of the educational goal of the report, it was also presented at the Aerospace Sciences Conference of the American Institute of Aeronautics and Astronautics on 25 January 1966, and is available as AIAA Preprint 66-64.

This report is released at the working level for information purposes and does not represent the final judgment of the Station.

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1. INTRODUCTION

1.1. GENERAL NATURE OF PROPELLANT IGNITION

Solid rocket propellants are made of materials or combinations of materials formed into plastic-like solid "charges" that burn inwards on their exposed surface during operation of the motor. The inward burning of the surface is governed by transfer of energy and chemically active species from the reaction zone. This process is approximately steady-state during most of the period of operation, i.e., the combustion consists of a constant-velocity wave progressing into the propellant mass. The wave is initiated by the application of energy and/or chemically active species to the propellant surface. The details of the transient propellant response to these initiation processes have thus far escaped complete elucidation, although it is increasingly evident that they differ conspicuously according to nature of the propellant, environmental condition, and nature of the initiating stimulus.

Solid propellants are chemically, and often physically, very complex. The prospect of resolving the chemical kinetic paths involved in ignition in any fundamental quantitative manner is very remote, although understanding of some dominant steps may be possible. An idea of the diversity of chemical paths involved is suggested by the diagram in Fig. 1.1. In this diagram, the ingredients of the propellant are depicted by the two upper circles, representing an oxidizer and a fuel (binder) present as a mixture, microscopically inhomogeneous. The third circle, at the bottom, represents chemically reactable materials in the surrounding environment. The rectangles in the diagram represent intermediate or final products in the reaction process, and the connecting lines represent idealized simple chemical interactions or transitions between ingredients, products, and environmental reactants. As arranged in the figure, the physical state of the reactants proceeds from solid to gas as one proceeds downward in the diagram, this representing the trend in the combustion zone in going from cold to hot side. In the event that the propellant is homogeneous, the diagrammatic representation requires only one of the upper circles.

Considering the variety of chemical materials used in propellants it seems clear that many types of ignition behavior will be encountered, which will not be encompassed in any single tractable theory. Ignition is often dominated by a thermal induction period in which a surface layer of the material is raised to a temperature at which chemical reaction rates are appreciable. This is followed by a runaway chemical

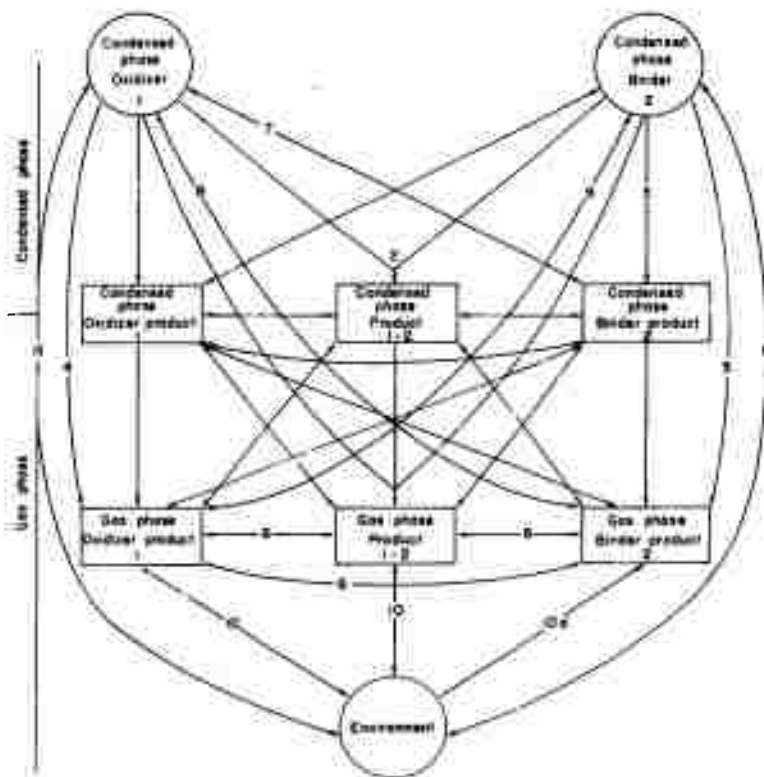


FIG. 1.1. Diagrammatic Representation of Some Classes of Reactions in a Composite Propellant. 1. Oxidizer decomposition to a solid or liquid - CONDENSED PHASE IGNITION THEORY. 2. Reaction between two condensed phase ingredients to a solid or liquid product - CONDENSED PHASE IGNITION THEORY. 3. Binder pyrolysis to solid intermediates - CONDENSED PHASE IGNITION THEORY. 4. Oxidizer decomposition to a gas. 5. Binder pyrolysis to a gas. 6. Gas phase diffusion flame of oxidizer and binder products. 7. Oxidizer interaction with solid binder intermediate products. 8. Heterogeneous reaction between condensed phase oxidizer and binder gases. 9. Heterogeneous reaction between solid binder and oxidizer gas - HETEROGENEOUS IGNITION THEORY. 10. Diffusion flame of propellant products with environmental oxidizer gas. 10a. Diffusion flame between binder gas products and environmental oxidizer gas - GAS-PHASE IGNITION THEORY. 11. Reaction between solid binder and environmental oxidizer gas - HYPERGOLIC IGNITION THEORY. Reaction between solid oxidizer and environmental binder gas.

process in which chemical self-heating quickly becomes the dominant heat source and ignition is achieved. When gas-phase reactions are required to sustain combustion, diffusion processes may delay ignition until appreciably after the onset of surface decomposition, imposing a further initiation requirement after thermal induction. In any case there is a natural tendency to seek out the exothermic reaction responsible for "runaway", and to then build an ignition theory centered around this "controlling" reaction. The construction of this report reflects this tendency, and the legend in Fig. 1.1 notes the types of reaction paths that are responsible for the principal ignition theories currently discussed in the literature.

1.2. EVOLUTION OF IGNITION THEORIES

Historically, the evolution of propellant ignition theory started with a bulk thermal explosion theory (e.g., Ref. 24). The first sophisticated attempt at a "surface-ignition" model was that of Hicks (Ref. 28), which led to a transient surface heating analysis with exothermic chemical heating in the solid with an exponential dependency of rate on temperature. The choice of this "solid-phase" model was made at a time when most propellants were of the colloidal nitrocellulose-nitroglycerin type which was known to undergo exothermic decomposition of the solid. Only limited experimental data were available to motivate consideration of a more complex model and the solid-phase model already taxed the capability of then available computers. Subsequent to the work of Hicks, other solid-phase models have been considered involving different assumptions regarding incident heating and nature of the self-heating (e.g., Ref. 9 and 43). Unique among the early works was Hicks's consideration of the thermal transient after removal of the "igniting stimulus." This aspect of the analysis was designed to test the "state-of-ignitedness" by the manner in which approach to steady-state proceeded, rather than by a superficial criterion for ignition, such as attainment of an "ignition temperature" at the surface.¹

The concept of a condensed-phase exothermic reaction is much less plausible in an ammonium perchlorate, rubber composite propellant, and consequently attention was soon directed to models involving participation of gas phase species in the exothermic reactions. A sequence of studies at Princeton University in the period 1956 to the present (Ref. 26 and 33) included development of a "gas-phase" model in which a hot oxidizing environmental gas and fuel vapors from the propellant mixed and reacted to provide a self-sustaining heat source. In this model

¹ Like most ignition models, that of Hicks did not actually encompass steady-state burning; his study of behavior after removal of the igniting stimulus was actually concerned with how long it would take for a runaway reaction to develop.

considerable attention is given to the concentration of oxidizer in the environmental gas because the propellants tested would not ignite in the original test apparatus unless the environmental gas contained oxygen. Accordingly, the analytical model represents the oxidizer as diffusing inwards toward the surface and the fuel as diffusing outwards from the surface, and only qualitative consideration is given to the case where both vapors originate at the surface of the heterogeneous propellant. Onset of ignition is defined by the attainment of a reversal in the gas-phase temperature trend or recovery of the temperature to some specified excess over the original gas temperature (without further assurance that removal of the igniting stimulus would leave a self-sustaining combustion wave).

A third body of propellant ignition theory was developed at the United Technology Center during the period 1962 to 1964 (Ref. 5). This theory evolved from studies of ignition by chemical activation of the propellant surface by powerful oxidizing gases such as fluorine. This hypergolic theory consists of a one-dimensional model with diffusion of vapor-phase species and with heat conduction into the solid and gas from the reaction surface. The sole source of heat is the heterogeneous surface reaction, which is assumed to obey an Arrhenius rate law. Attainment of ignition is judged in the model to have been realized when some arbitrarily selected high rate of temperature rise at the surface is attained. In the hypergolic theory, primary emphasis is given to the effect of concentration of the oxidizer, and it is argued that the effect of concentration on the ignition delay observed experimentally is consistent with the hypergolic theory. The argument is extended on a heuristic basis to encompass ignition by external heating of heterogeneous propellants in an inert environmental gas (Ref. 7, 14). In this "heterogeneous ignition theory," it is argued that the oxidizer is decomposed by external heating and that the resulting gaseous products attack the fuel surface as in hypergolic ignition. No analytical representation is made of this sequence of external heating - oxidizer decomposition - oxidizer product diffusion - heterogeneous fuel oxidation.²

To this date an adequate comparison of the theories has been obstructed by the incompleteness of the analytical models insofar as ignition of heterogeneous propellants in neutral atmospheres with external heating is concerned. The heterogeneous theory does not include any quantitative representation of external heating,² and thus application is restricted to an oxidizing environment that is hypergolic, i.e., self-igniting at room temperature. The boundary conditions for heating of the solid are different in the gas-phase model than in the solid-phase model, making comparison of analyses, or of any particular experimental result with both theories, of doubtful significance. Neither of these theories contains an analytical representation of the decomposition of the oxidizer or the subsequent three-dimensional diffusion of the oxidizer products to the fuel surface. The solid-phase theory is not consistent with current views regarding the nature of

² Reference 14 purports to include such representation, but details provided are not sufficient to determine what was actually done.

ammonium perchlorate decomposition, and not consistent with the observation of pressure dependence of the ignition process. These and other points will be more evident in the following sections of the report, and should be matters of concern in all discussions regarding the physical relevance of the different theories and the current ability to test relevance by experiment.

1.3. MEANING OF "IGNITION" AND ROLE OF THE CHEMICAL "RUNAWAY"

The attainment of a steady-state deflagration wave is an asymptotic process, and a definition of the attainment of ignition has consequently been a source of continuing difficulty, meriting early attention in a review. From a practical viewpoint the principal issues are how much stimulus, e.g., energy, must be supplied to produce a self-sustaining deflagration, and how long will it take before steady-state is approached? Experimentally, attainment of ignition is judged by criteria such as observation of the first onset of self-luminosity, observation of some state of pressure rise, or demonstration of first attainment of self-sustaining reaction upon removal of initiating stimulus. These "tests" are all susceptible to quantitative application in one experiment or another, but do not always give the same results in the same ignition experiment. Thus, intelligent use of the data is compromised by lack of a widely accepted and applicable quantitative definition of ignition.

The problem of definition and measurement of the attainment of ignition is considerably alleviated in a practical sense by the fact that chemical processes are exponentially rate dependent on temperature. As a result it is often true that all of the chemical reactions associated with ignition occur precipitously at the very end of a period of external heating and all of the experimental techniques would then indicate nearly the same "moment-of-ignition," which would reflect primarily the fulfillment of "thermal induction" requirements for attainment of "runaway" exothermic reaction (often associated with a characteristic "ignition temperature").

The effect of the exponential temperature dependence of the reaction rate on the character of the ignition process is illustrated by reference to a family of solutions to the condensed phase theory in Fig. 1.2 (see also Section 2.2.3.2. or Ref. 17), which shows solutions to the one-dimensional heat conduction problem for a surface heated semi-infinite slab including an exponentially temperature dependent heat source in the solid. The solid lines in the figure correspond to externally supplied heats (q) required to yield specified surface temperature rise (as a function of \dot{q}), and the dotted lines represent the total externally supplied heat added by a specified time (as a function of \dot{q}). Considering an ignition event involving a particular external heating rate, the temperature rises along the corresponding \dot{q} ordinate line, with the

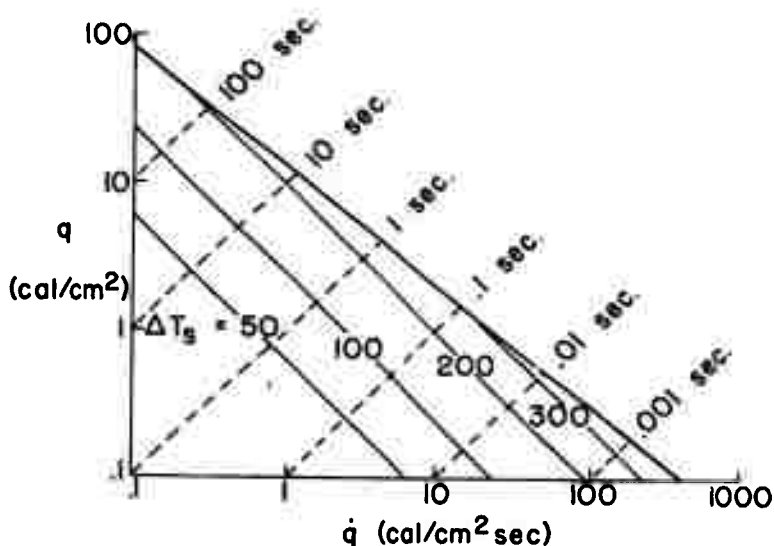


FIG. 1.2. Solutions of One-Dimensional Condensed-Phase Heat Conduction Problem for Constant Surface Heat Flux and Internal Heat Generation Equal to $B_c \exp(-E_c/RT)$. ($B_c = 10^{22}$ cal/cm³ sec; $E_c/R = 25,000^\circ\text{K}$; $\rho_c = 1.6$ gm/cm³; $c_c = 0.37$ cal/gm^oK; $k_c = 5 \times 10^{-4}$ cal/cm sec^oK).

successive temperatures indicated by the ΔT_s grid and the time indicated by the t grid. As the temperature reaches a value conducive to chemical self-heating, the temperature rises very rapidly (i.e., with very little added heating time) due to the rapid self-heating. Any specified further rise in surface temperature is attained in negligible time due to the exponential dependence of the self-heating rate on the rising temperature. This is reflected in the compression of the constant ΔT_s lines to an upper limit at each \dot{q} , determining a limit curve which would conform to a condition of "ignitedness" by almost any criterion. The abruptness of the compression of the ΔT_s lines reflects the rapidity with which self-heating becomes dominant, and in some cases makes the detailed study of the chemical heating phase of the ignition unimportant insofar as q or ignition delay are concerned.

Continuing for simplicity with the condensed-phase theory, it should be noted that, while possessing considerable intuitive appeal, there was nothing rigorous about the view that ignition was consummated at the moment of approach to the limit line in Fig. 1.2. Indeed, it has been

widely assumed to the contrary that ignition is attained at some characteristic critical or "auto-ignition" temperature, associated presumably with some critical reaction rate. This issue has been belabored at length by various investigators, and it seems quite clear that no universally applicable definition of attainment of ignition is available. The problem is examined carefully by Hicks (Ref. 28) for the case of condensed-phase thermal theory for semi-infinite slabs, where the concept of an auto-ignition temperature is rejected, and a criterion is set up for ignition involving behavior of the heated surface following interruption of the external heating. It is noted that, upon cessation of external heating, the surface temperature may either continue to rise, or may initially fall, depending on the dominance of heat loss inwards from the surface, or of heat generation at the surface. The criterion selected by Hicks (and later generalized by Baer, Ref. 10) can be shown to be related to approach to the limit curve in Fig. 1.2, which assures that, regardless of original external heating rate, the chemical heating rate will be large enough to override the quenching effect of the temperature gradient produced during the external heating. Thus, in terms of the interrupted heating test of ignition, approach to the limit line in Fig. 1.2 appears to be a better measure of ignition than an "auto-ignition" temperature. However, it is not always feasible to interrupt the initiating stimulus in ignition experiments, so that definitions of ignition based on other criteria may be anticipated.

1.4. CONCEPT OF IGNITION BY SURFACE AND GAS-PHASE REACTIONS

When the exothermic reactions controlling ignition involve gas-phase species, the reaction rates necessarily involve the concentration of reactants, and ignition times are correspondingly dependent on concentration. The extent to which this modifies the arguments of the last section is probably unknown at present. There is a tendency for ignition to take longer because the reaction sites are less favorably situated to act as heat sources for sustaining decomposition of the solid propellant, and because some diffusion time may be required before gas-phase species are present in concentrations requisite for self-sustained heating. So long as the exothermic reaction is controlled ultimately by an exponential temperature dependence (and not by diffusion or convective transport of reactants), it would not matter that the reaction was a heterogeneous or gas phase one at or very near the surface. The chemical reaction would be accelerated very rapidly once started, because the external heating would assure rapid attainment of the relatively small additional temperature rise required for a precipitous chemical runaway as in the solid-phase theory. Details of definition and measurement of onset of ignition would remain non-critical as in the solid-phase theory, all reasonable choices leading to nearly the same (pressure-independent) ignition time at any particular heating rate. If, on the other hand, self-sustaining or runaway conditions are limited initially by diffusion processes in the gas layer,

the exponential temperature dependence of reaction rates is not dominant in the transient behavior at the onset of gassification. In that case, external heating may be sustained for some time after onset of reactions without experiencing a self-sustaining or runaway condition. During this period, propellant products will diffuse outwards (or convect outwards if the heating rate is high enough), and exothermic reactions will build up as favorable concentrations develop. Being poorly situated to communicate heat to the solid, these reactions do not maintain their own supply of reactants easily, and the supply may be interrupted by thermal quenching when the external heating is shut off. In the present descriptive framework of external heating followed by concurrent heating and reaction, no relevant gas-phase theory has been published,³ so that descriptions of the ignition process in this framework are speculative, and comparisons of theory and experiment are impossible. However, the qualitative considerations of diffusion limited processes and reaction sites removed from the solid offer a basis for explanation of the pressure dependence of ignition at high heating rates.

Consideration of appropriate criteria for ignition in gas-phase-limited ignition situations has received little attention, the only relevant discussions being those of Ref. 26 and 33 in the context of a constant-surface-temperature model. Experimental work relevant to this model used the onset of radiation as a criterion, while Ref. 10, 12, 14, and 17 describe other methods considered. Testing in arc-image furnaces is more consistent with the "sequential processes" description (thermal induction-chemical heating) used above, with experimental criteria including both radiation detection and go no-go tests. In the domain of high heating rate and low pressure, the radiation detection method is unreliable because (Ref. 12, 13, 14, and 29) of the evolution of light-scattering propellant products long before self-sustaining conditions are achieved. This observation is suggestive of diffusion-controlled reactions, since sustained decomposition occurs at the surface before self-sustaining conditions are achieved.

1.5. "PROOF" OF IGNITION THEORIES

Recent developments of ignition theory have been accompanied by considerable debate, claims of decisive achievement and claims of experimental verification. As deeper insight evolves from these adventures, it becomes increasingly evident that the accuracy of the experimental data is not sufficient to test the theories (Ref. 29), the theories themselves do not provide quantitative predictions relevant to the experiments, and the formulations of the theories are such that

³The theory of Ref. 26 and 33 is based on conductive heating, with surface temperature and decomposition rate taken to be constant from the start of heating. A subsequent, unpublished analysis by the authors of Ref. 26 (see Ref. 27) considers a step rise in surface temperature followed by continued temperature rise due to conductive heating.

they cannot all be tested by the same experiment. Further, the individual investigators have usually been too preoccupied with agreement between theory and experiment to explore the quality of agreement afforded by alternate theories.

By reviewing the published theories here in a single report with a common notation for all, it is hoped that a better perspective for future work will be provided, and that the domain of relevance of various theories may be more quickly identified. Proof of a theory - any theory - consists of a consensus among knowledgeable scientists. The present state of ignition theory is far from that.

2. SOLID-PHASE THERMAL THEORY

The solid-phase thermal theory, to be considered here, is distinguished by (1) absence of mass diffusion arising from concentration or thermal gradients and (2) insensitivity to conditions in the surrounding gas phase except as they affect thermal properties of the surrounding gas and ensuing heat loss. Often, the depletion of reactable material is also ignored, but a separate equation for this effect is included in the present analysis. In the case of a semi-infinite solid and one-dimensional heat flow, the field equations and boundary conditions for solid-phase thermal theory can be written as follows:

$$\begin{array}{cccc} \text{I} & \text{II} & \text{III} & \text{IV} \\ \rho_c c_c (\partial T / \partial t) = k_c (\partial^2 T / \partial x^2) + \rho_c c_c r (\partial T / \partial x) + \beta \dot{q} \exp(-\beta x) & & & \\ & \text{V} & & \\ & + Z_c Q_c C_i^a r^a \exp(-E_c / RT) & & \end{array} \quad (2.1)$$

$$\partial f / \partial t = -Z_c C_i^{a-1} r^a \exp(-E_c / RT) \quad (2.2)$$

$$\dot{q}_n + \dot{Q}_s = -k_c (\partial T / \partial x) \quad \text{at } x = 0 \quad (2.3)$$

$$T = T_i \quad \text{at } t = 0 \quad (2.4)$$

$$T = T_{\infty} \equiv T_i \quad \text{at } x = \infty \quad (2.5)$$

or

$$(\partial T / \partial x) = 0 \quad \text{at } x = \infty \quad (2.5a)$$

$$f = 1 \quad \text{at } t = 0 \quad (2.6)$$

\dot{q} , \dot{Q}_s , and \dot{q}_n are in general functions of time and/or temperature.

In Eq. 2.1 the different terms have the following physical interpretations:

- I. Rate of accumulation of energy
- II. Rate of energy gain by thermal conduction in the solid
- III. Rate of energy convection due to motion of the surface (introduced mathematically by transformation of coordinates from stationary to moving system)
- IV. Rate of absorption of energy in depth due to optical transparency of solid
- V. Rate of chemical heat generation by an effective a^{th} order reaction. (If more than one chemical reaction is considered, a term must be included for each.)

Equation 2.2 is the rate equation for a chemical reaction of order "a", where C_i is the initial concentration of reactant and f is the fraction of reactant remaining at any time. Equation 2.3 is the heat balance at the moving boundary, $x = 0$. The term \dot{q} represents any energy transferred between the surface and the surroundings by virtue of thermal gradients. The term \dot{Q}_s represents heat sources associated with the surface and includes chemical reactions as well as heats of phase change. The derivative term represents heat conducted into the solid. Equation 2.4 expresses the initial condition, usually taken as constant temperature. In cases where the temperature-time history is required after cessation of a pulse of energy, the initial condition for the period following heating will be the temperature distribution at the end of the pulse. The boundary condition at infinity can be taken as a given temperature for the case where there is no distributed chemical reaction or as zero gradient when chemical reaction is present. The two alternatives are practically equivalent for times before the rate of chemical reaction becomes significant.

In the derivation of the foregoing set of equations, a number of simplifying and often unrealistic assumptions was made. First, it is common to regard the physical properties (ρ , c , k , β , and Q) as constants. Actually, there are several conditions which could have a severe effect on this assumption: (1) the heterogeneity of some propellants with different physical properties for each constituent, (2) temperature dependence of physical (including optical) properties, (3) time dependence of physical properties due to changing composition, and (4) the dependence of β upon the spectral distribution of radiant energy.

The second assumption is that of one-dimensional heat conduction which, in the case of heterogeneous propellant, would require close scrutiny. The assumption of the semi-infinite slab should also be examined in cases of experiments on thin samples. Finally, the representation of the complex chemistry involved by a simple Arrhenius reaction rate term or series of such terms is a gross simplification which reflects considerable ignorance of what is actually occurring. In addition, the definition of the surface and its motion is complicated by the fact that it is often not a mathematical plane but a seething, bubbling region of finite and time-dependent dimensions. In steady-state, at least the velocity of motion of the surface may be defined adequately in terms of a particular point on the temperature profile which moves at the same rate as the "surface." However, under transient conditions present during ignition, the temperature profile constantly changes relative to the "surface," as does the physical character of the surface region, and no such definition is accurate. With no precise definition of the location of the surface, the meanings of the various terms in Eq. 2.3 become uncertain.

Despite the difficulties of representing the complex ignition phenomenon by a mathematically tractable set of equations, theoretical studies have been made using various combinations of Eq. 2.1-2.6. It will be noted that the equations are highly nonlinear because of the exponential reaction rate term. The motion of the surface also introduces a nonlinearity (Ref. 20, p. 284) in the transient case. These mathematical difficulties can be resolved only through use of numerical analysis - which tends to obscure the trend of results, or by linearization procedures - which often eliminates important factors from consideration. In addition, one fundamental difficulty faces not only the theoretician, but the experimentalist, viz., the definition of ignition. Theoretically, ignition may be and has been regarded as having occurred when: (1) the surface temperature reaches a critical value, the so-called auto-ignition or critical ignition temperature, (2) the rate of rise of surface temperature reaches a certain value, (3) the rate of evolution of reactable gases from the surface reaches a certain level, or (4) after cessation of application of the ignition stimulus, the surface temperature (which may initially decrease) eventually undergoes a precipitous rise. The time of occurrence of this precipitous rise is frequently not specified, but should be included as a part of the criterion. Without such a time criterion, a

semi-infinite solid with no depletion of reactants may be considered as ignited whenever the initial temperature is above 0°K . Experimentally the ignition event has been determined from surface or subsurface temperature measurements, radiation measurements, pressure measurements, and observations made on a propellant sample after shutoff of the ignition stimulus. No complete study of the interrelationships of these various criteria has been made. Additional experimental difficulties exist which complicate the interpretation of experimental results in the light of theory. These include uncertainty as to the rate of heat transfer owing to the use of steady-state film coefficients in cases of convective heat flow, and of changes in surface conditions and surrounding gas properties when the igniting source is radiation flux.

In the effort to solve Eq. 2.1-2.6, certain concessions have been made by various investigators which permit analytical solution or reduce the number of parameters involved in the case of numerical analysis. Advantage is usually taken of nondimensional parameters and variables. A number of solutions are obtained by ignoring terms III and IV and either I or II in Eq. 2.1, and neglecting depletion of reactants. The solutions so obtained, viz., those of Semenov and Frank-Kamenetskii, are applicable to systems in which the temperature either rises relatively slowly until ignition (DTA) or is space uniform (well stirred reactor). Even when the effect of reactant depletion is considered (Ref. 49), these special solutions have little if any applicability to solid propellant ignition, in which a thermal wave (space and time dependent) is propagated as a result of the ignition stimulus. Mention is made here of these cases in order to include them in the morphological study of Eq. 2.1-2.6, but no further discussion of them is proposed. Numerical steady-state solutions of Eq. 2.1 have also been obtained in which reactant depletion is the only effect neglected (Ref. 39). These results are of use in the ignition field principally for the purpose of establishing a steady-state temperature profile for comparison with transient profiles occurring during ignition.

The numerous possible solutions of special cases of Eq. 2.1-2.6 can be catalogued according to which terms are retained in the field equations (Eq. 2.1-2.2) and according to the boundary conditions. All combinations have not been explored. Indeed, it is not obvious that every case is of equal interest relative to ignition studies. In those cases which have received consideration, the choice has often been motivated by mathematical simplicity and/or relevance to a particular experimental situation. In several instances the agreement between the conditions of the mathematical model and the conditions of the experiment is questionable. In the following sections the salient features of several of the more relevant theories are presented. These theories are classified according to whether or not chemical heating terms are included in the fundamental equations.

2.1. HEATING OF AN INERT SOLID

A starting point for many ignition theories is the solution of the heat conduction equations for a solid material containing no chemical heating term. This simplification often leads to analytical solutions, but it must be emphasized that the model contains in itself no basis for judging the attainment of an ignited state. After cessation of the ignition stimulus, energy to sustain the ignition transient must be supplied by gas phase or heterogeneous reactions, or by previously ignored condensed phase reactions; otherwise, the solid-phase temperature would decay and no ignition would occur. It is common and convenient practice to ignore the details of such external reactions and to characterize ignition as having occurred when the surface temperature reaches a particular value referred to as the critical ignition temperature. The solutions presented for inert models are based upon this fundamental premise. It is important to note, however, that the success of exothermic reactions in producing ignition is contingent upon the nature of these reactions, how heat is transferred back to the solid, the geometry of the system and upon the history of the initial heating of the solid. The correlation of these multiple phenomena in terms of a single parameter, viz., the critical ignition temperature, would not seem reasonable unless substantiated by a more complete analysis involving processes occurring in the gas phase as well as in the solid phase. The use of a constant, critical ignition temperature can only be regarded as a simplification made in lieu of dealing with a more complete model. If the processes occurring between time of attainment of this temperature and time for self-sustaining reaction occupy little time relative to the initial heating period (the theory for inert solids contains no provision for calculating the additional time) then the critical ignition temperature is a useful parameter, and only then can the simple heating model represent an ignition theory.

2.1.1. Stationary Boundary and Opaque Solid.

The simplest solution of Eq. 2.1-2.6 is obtainable under the assumptions that the material subjected to the energy pulse is completely opaque and that the boundary does not move. The solution depends upon the boundary condition at the heated surface, which in turn is controlled by the mode of heating. The cases most often considered are: (1) maintenance of a constant surface temperature with no film drop, (2) heating by radiant flux of known time dependence, and (3) heating by a constant source temperature with a film drop, usually taken as represented by a constant film coefficient.

2.1.1.1. Constant Surface Temperature With No Film Drop.

A constant interface temperature is obtained if two inert semi-infinite slabs, each at a uniform temperature, are brought into intimate contact. An attempt to reproduce this boundary condition experimentally is found in the so-called "hot-plate" experiments, in which the propellant sample is suddenly brought into contact with a heated metal block.

The interface temperature, which is attained immediately upon contact, is intermediate to the two initial uniform temperatures and is given by Ref. 20, p. 88.

$$(T_s - T_i)/(T_b - T_i) = [1 + (\rho_c c_c k_c / \rho_b c_b k_b)^{\frac{1}{2}}]^{-1} \quad (2.7)$$

where the subscript "b" denotes the block. Under ideal conditions of perfect contact and no gas evolution, one might expect to find a critical hot-plate temperature above which ignition occurs instantly and below which ignition never occurs, provided the critical ignition temperature is a valid concept. No such results are in evidence; moreover, interpretation of the experimental data is complicated by uncertainty as to both the assumptions of constant critical surface temperature and no film drop. The existence of a gas film is qualitatively consistent with the experimental effect of gas pressure on the relationship between ignition time and block temperature (Ref. 55). By ignoring the film drop and introducing a solid-phase chemical reaction, the results may also be explained (See section 2.2.1.).

2.1.1.2. Radiant Heating. The equations corresponding to case (2) are:

$$\rho_c c_c (\partial T / \partial t) = k_c (\partial^2 T / \partial x^2) \quad (2.8)$$

$$T = T_i \quad \text{at } t = 0 \quad (2.9)$$

$$T = T_\infty \equiv T_i \quad \text{at } x = \infty \quad (2.10)$$

$$\dot{q} = -k_c (\partial T / \partial x) \quad \text{at } x = 0 \quad (2.11)$$

where it is emphasized that \dot{q} represents all non-reflected radiant energy arriving at the propellant surface. The solution of Eq. 2.8-2.11 for $\dot{q} = \text{constant}$ (the usual goal in arc-image experiments) is (Ref. 20, p. 75).

$$T - T_i = (2\dot{q} \sqrt{\alpha_c t} / k_c) \operatorname{ierfc}(x/2 \sqrt{\alpha_c t}) \quad (2.12)$$

which gives for the surface temperature rise

$$\Delta T_s = T_s - T_i = 2\dot{q} \sqrt{t / \pi k_c \rho_c c_c} \quad (2.13)$$

The total energy supplied during the time interval t is

$$q = \int_0^t \dot{q} dt = \dot{q} t \quad (2.14)$$

Eliminating t from Eq. 2.13 and 2.14, we have

$$q \dot{q} = \pi k_c \rho_c c_c (\Delta T_s)^2 / 4 \quad (2.15)$$

In Fig. 2.1, Eq. 2.14 and 2.15 are depicted graphically on a $\log q$ vs. $\log \dot{q}$ plot. Lines of constant time are indicated as dotted while lines of constant surface temperature rise (ΔT_s) are shown solid. When experimentally determined ignition data are plotted as $\log q$ vs. $\log \dot{q}$, straight lines with a slope of minus one are sometimes obtained (especially in the case of composite propellants at low heating rates and high pressures). Such agreement of experiment with theory has been interpreted as substantiating the concept of critical ignition temperature and has been used to infer the value of this temperature as well as the thermal properties of the propellant.

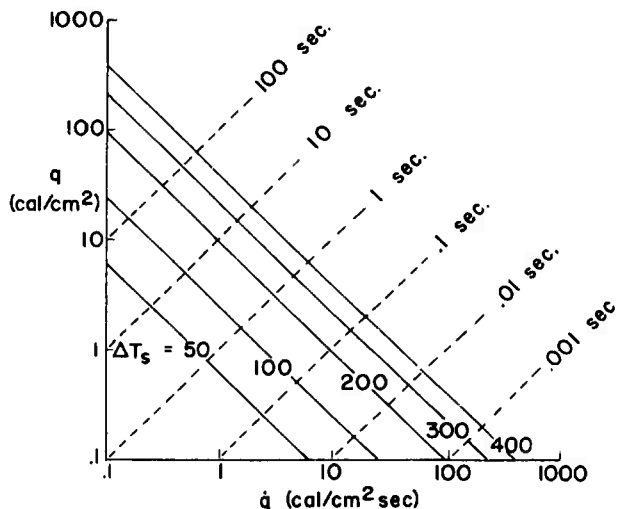


FIG. 2.1. Solutions of One-Dimensional Heating of Condensed Phase, Inert Material.

($\rho_c = 1.6 \text{ gm/cm}^3$; $c_c = 0.37 \text{ cal/gm}^\circ\text{K}$; $k_c = 5 \times 10^{-4} \text{ cal/cm sec}^\circ\text{K}$).

In the discussion of radiant heating, it has been assumed thus far that \dot{q} and the thermal properties of the propellant are constants and that no heat is lost to the surroundings during the heating period. It is of interest to examine the effect of relaxing one or more of these assumptions. Again, the discussion is in terms of lines representing constant surface temperature on a $\log q$ vs. $\log \dot{q}$ diagram.

2.1.1.2.1. Heat loss to surroundings by conduction. In arc-image experiments, heating is often accomplished in the presence of a gaseous atmosphere. Insofar as heat losses are conductive (for short heating times where convection currents have not yet been established), and the gas may be considered semi-infinite, the mathematical model consists of a set of equations similar to Eq. 2.8-2.11 for each phase. The final solution (based on Ref. 20, p. 88) indicates that for a given surface temperature rise ΔT_s , the product $q\dot{q}$ is increased from the value given by Eq. 2.15, by the factor

$$\chi = [1 + (k_g \rho_g c_g / k_c \rho_c c_c)^{\frac{1}{2}}]^2 \quad (2.16)$$

The relationship between q and \dot{q} is thus altered only to the extent that the positions of the isotherms on the $\log q$ vs. $\log \dot{q}$ diagram are changed with no effect on the slope. A short table of typical values of $\chi-1$ is given in Ref. 43, indicating that, depending upon properties of the surrounding gas, there is an increase in energy required due to heat loss by this mechanism of approximately 2 percent at one atmosphere to 15 percent at 100 atmospheres.

2.1.1.2.2. Heat loss to surroundings by convection. With longer times or forced flow, the heat loss to the surrounding gas is by convection, with the governing equations being as follows:

$$\rho_c c_c (\partial T / \partial t) = k_c (\partial^2 T / \partial x^2) \quad (2.17)$$

$$T = T_1 \quad \text{at } t = 0 \quad (2.18)$$

$$T = T_\infty \equiv T_1 \quad \text{at } x = \infty \quad (2.19)$$

$$-k_c (\partial T / \partial x) = \dot{q} - H (T - T_1) \quad \text{at } x = 0 \quad (2.20)$$

It is assumed for convenience that the temperature of the gas remains constant at the same value as the initial temperature of the solid, hence, that it is not heated appreciably during the period of interest. In addition, the film coefficient for convective heat loss is taken

as constant. The solution of Eq. 2.17-2.20 for constant \dot{q} is

$$1/G_1 = 1 - \exp(G_2/G_1) \operatorname{erfc} \sqrt{G_2 G_1} \quad (2.21)$$

where G_1 represents the group $(\dot{q}/H\Delta T_s)$ and G_2 represents the group $(qH/k_c \rho_c c_c \Delta T_s)$. It is evident from Eq. 2.21 that a constant surface temperature rise is not characterized by a constant $q\dot{q}$ product. It can be argued physically and demonstrated analytically that the effect of convective loss on the $\log q$ vs. $\log \dot{q}$ relation is to raise the value of q at lower values of \dot{q} (longer heating times). Larger values of H would increase the relative heat loss to the gas and would cause the constant ΔT_s curves to depart even more from a slope of minus one. The effect is depicted in Fig. 2.2 for ΔT_s at 200°C and values of H selected to represent heat loss by natural or forced convection. It is seen that for the example chosen the effect of convective heat loss is marginally significant for forced convection. Curves for other values of the parameters may be obtained if it is noted that Fig. 2.2 was derived from a universal relationship between $(qH/k_c \rho_c c_c \Delta T_s)$ and $(\dot{q}/H\Delta T_s)$.

2.1.1.2.3. Variable thermal properties. Over the range of temperatures involved in ignition, it is likely that the various thermal properties are not constant. However, the thermal diffusivity α_c ($\equiv k_c/\rho_c c_c$) frequently is less sensitive to temperature changes than conductivity or specific heat alone (Ref. 20, p. 11). In such cases of constant α_c , it can be shown by the techniques of Ref. 20 that for a given surface temperature rise, the product $q\dot{q}$ is constant, although not the same constant as for invariant thermal properties. In addition, the surface temperature rise is influenced by the initial propellant temperature. It must be remarked that variable thermal properties may also be a consequence of reactant consumption or decomposition (not considered here) in which case the effect on the product $q\dot{q}$ for constant ΔT_s has not been determined.

2.1.1.2.4. Variable flux. Even though efforts are made to assure constant radiant flux in arc-image experiments, there are circumstances under which the flux absorbed by the propellant varies because of variations in optical properties of the intervening medium and the propellant surface. The variation of flux with time is seldom known; nevertheless, it is of interest to examine the effect of arbitrarily chosen time variations which may approximate real cases. One of these variations is

$$\dot{q} \propto t^{5/2} \quad (2.22)$$

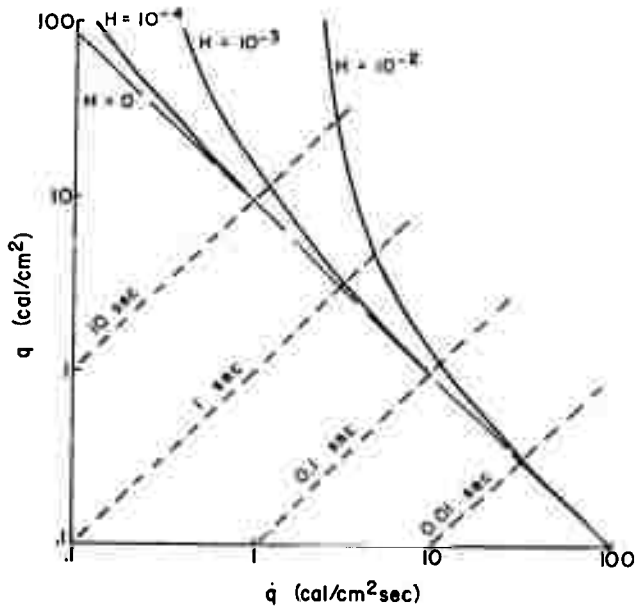


FIG. 2.2. Effect of Surface Convective Heat Loss on Surface Isotherms for Radiant Heating of an Opaque Inert Solid.

($\Delta T_s = 200^\circ\text{K}$; $k_c = 5 \times 10^{-4}$ cal/cm sec $^\circ\text{K}$; $\rho_c = 1.6$ gm/cm³; $c_c = 0.37$ cal/gm $^\circ\text{K}$; H given in cal/cm² sec $^\circ\text{K}$).

with the solution (using the results of Ref. 20, p. 77)

$$q\dot{q}_t = k_c \rho_c c_c (\Delta T_s)^2 f'(\tau) \quad (2.23)$$

The term \dot{q}_t is the value of the flux at the end of the heating period when the surface temperature has risen by ΔT_s . The function $f(\tau)$ assumes the value $\pi/4$ for $\tau = 0$ (constant \dot{q}) and increases with increasing τ . It is seen from the form of Eq. 2.23 that, for a given surface temperature rise, the graph of $\log q$ vs. $\log \dot{q}_t$ is a straight line with a slope of minus one. The statement can be shown to be equally true if the average value of \dot{q} over the heating time is used instead of \dot{q}_t . The usefulness of this result is of course contingent upon the relevance of a critical ignition temperature in the case of the assumed flux-time relationship.

Another mathematically simple flux variation is given by $\dot{q} = \dot{q}_i e^{-dt}$, where \dot{q}_i is the initial value of an exponentially decaying flux. Such a function might represent the case where smoke and other absorbent products are evolved during the heating period. The solution of the equations under this boundary condition may be obtained in terms of tabulated functions (Ref. 20, p. 64) and indicates that an isotherm in the $\log q$ vs. $\log \dot{q}_{av}$ diagram would depart from the isotherm for the case of constant \dot{q} . The greatest deviation would be for long heating times (low fluxes), with a higher q being required for the variable \dot{q} case.

2.1.1.3. Constant Gas Temperature and Constant Film Coefficient. This case is often taken as representative of heating by hot gases. Except for recent efforts (Ref. 30 and 38) the heat flux is usually not measured; instead, use is made of gas film heat transfer coefficients estimated on the basis of steady-state correlations for free- and forced-convective heat transfer to an inert surface (Ref. 44). The solution for the surface temperature is

$$(T_s - T_i)/(T_g - T_i) = 1 - \exp(h^2 a_c t) \operatorname{erfc} \sqrt{h^2 a_c t} \quad (2.24)$$

Inasmuch as the surface temperature is variable while gas temperature and film coefficient are assumed constant, the heat flux is also variable. However, it can be shown (Ref. 51) that for a given surface temperature rise, the product of q and average \dot{q} is nearly constant even when the surface temperature rise is as great as one-third the initial temperature difference between the gas and the solid. The effect is an increase of one or two percent in the magnitude of the slope of the surface isotherm in the $\log q$ vs. $\log \dot{q}_{av}$ diagram. The relevance of this treatment is uncertain to the extent that the film coefficient is not likely to remain constant during transient conditions.

2.1.2. Stationary Boundary with Optical Absorption of Energy in Depth:

In the preceding discussion the solid has been assumed to be completely opaque. However, in many instances of radiant heating, energy impinging upon the surface penetrates instantaneously according to Beer's law of exponential decay and subsequently undergoes thermal conduction. For this case the following set of equations is obtained:

$$\rho_c c_c (\partial T / \partial t) = k_c (\partial^2 T / \partial x^2) + \beta \dot{q} \exp(-\beta x) \quad (2.25)$$

$$T = T_i \quad \text{at } t = 0 \quad (2.26)$$

$$T = T_\infty \equiv T_i \quad \text{at } x = \infty \quad (2.27)$$

$$(\partial T / \partial x) = 0 \quad \text{at } x = 0 \quad (2.28)$$

with the solution (Ref. 38).

$$1/G_3 = (2/\sqrt{\pi}) \sqrt{G_4/G_3} + \exp(G_4/G_3) \operatorname{erfc} \sqrt{G_4/G_3} - 1 \quad (2.29)$$

where G_3 represents the group $(\dot{q}/\beta k_c \Delta T_s)$ and G_4 represents the group $(q\beta/\rho_c c_c \Delta T_s)$. The complicated manner in which q and \dot{q} are involved indicates that for a given surface temperature rise, the product $q\dot{q}$ is not constant. The absorption of radiation in depth would be expected to affect the surface isotherms in the $\log q$ vs. $\log \dot{q}$ plane mainly at high heating rates where heat transmission by conduction is limited by the short time (Ref. 15 and 16). The effect is to increase the quantity of heat required to raise the surface temperature by a given increment. At extremely high heating rates, the time available for heat conduction would be so small that the temperature profile would be determined almost exclusively by radiant absorption. The increase in surface temperature would then be determined by the total amount of heat applied and the absorptivity β in accordance with the solution of the differential equation from which the term $k_c (\partial^2 T / \partial x^2)$ is omitted.

$$\Delta T_s = \beta q / \rho_c c_c \quad (2.30)$$

An alternate interpretation of Eq. 2.30 is that β represents a lower limit of absorptivity, below which a given amount of energy, q , no matter how rapidly applied, is insufficient to raise the surface temperature by a preassigned increment, ΔT_s (Ref. 41). At very low heating rates, the effect of absorption would be of diminishing importance and the relation of q vs. \dot{q} would approach the solution for complete opacity. Figure 2.3 shows the effect of radiant absorption for values of β of 10, 100, and 1000 cm^{-1} , which are typical of oxidizer crystals, light colored double-base propellants and darkened double-base propellants, respectively. Curves for other values of the parameters may be obtained if it is noted that Fig. 2.3 is derived from a universal relationship between $(q\beta/\rho_c c_c \Delta T_s)$ and $(\dot{q}/\beta k_c \Delta T_s)$.

2.1.3. Moving Boundary and Opaque Solid.

In the event that the energy falling upon the propellant surface causes a marked change in physical or chemical properties (e.g., through evaporation or chemical reaction), then the ensuing motion of the line of demarcation between the regions of different properties leads to a relatively complicated situation known as the moving boundary or Stefan problem. In only a few instances has this effect been studied or even included in a treatment of solid propellant ignition. This neglect is probably attributable to several reasons. First, is the difficulty of representing the moving boundary adequately either conceptually or mathematically because subsurface conditions are necessarily complicated by boundary movement. Second, is the mathematical complexity introduced. Third, is the rationalization that propellant ignition is achieved prior to any appreciable decomposition of the propellant and subsequent motion of the surface. The same reasoning is frequently applied in order to rationalize neglect of chemical reactions. While the situation is relatively clear in cases of explosives (where the effect of reactant consumption and boundary movement is minimum, Ref. 21), and in wood burning (where the effect may be controlling, Ref. 45 and 49), propellants would represent intermediate situations requiring further study.

An extensive numerical analysis has been carried out (Ref. 31) for the case of constant surface temperature and constant latent heat of phase change. The equations considered were (in the notation of the present report)

$$\rho_c c_c (\partial T / \partial t) = k_c (\partial^2 T / \partial x^2) + \rho_c c_c r (\partial T / \partial x) \quad (2.31)$$

$$\dot{q} = -k_c (\partial T / \partial x) - \rho_c c_c r \quad \text{at } x = 0 \quad (2.32)$$

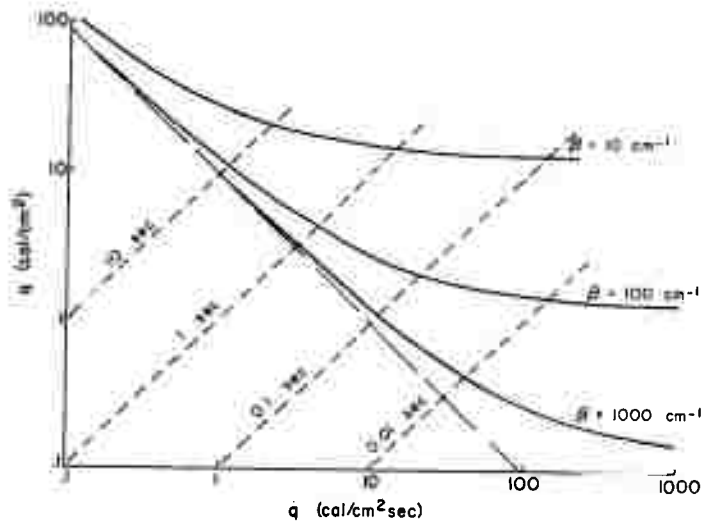


FIG. 2.3. Effect of Transparency of Solid on Surface Isotherms for Radiant Heating of an Inert Solid With No Surface Heat Loss. (ΔT_s , k_c , ρ_c , and c_c as in Fig. 2.1).

$$T = T_i \quad \text{at } t = 0 \quad (2.33)$$

$$T = T_\infty \equiv T_i \quad \text{at } x = \infty \quad (2.34)$$

The solution was applied to the case of a solid propellant (Ref. 40) and indicates that for reasonable values of constants (a) the surface temperature gradient during steady-state burning is less than at any time leading up to steady-state conditions and (b) the heat stored in the propellant above ambient temperature is greater during steady-state than at the onset of pyrolysis. The relation between the heat stored under the two conditions can be obtained from the steady-state solution of Eq. 2.31-2.34, viz.,

$$(T - T_i)/(T_s - T_i) = \exp [-\dot{q} c_c x / k_c (-Q_m + c_c \Delta T_s)] \quad (2.35)$$

which upon integration gives

$$q_{ss} = \rho_c c_c k_c (\Delta T_s)^2 [1 - (Q_m / c_c \Delta T_s)] / \dot{q} \quad (2.36)$$

where Q_m is the latent heat of phase change, negative for melting or other endothermic processes. Comparison of the heat stored at steady-state, q_{ss} , with the heat stored at the onset of pyrolysis

$$q^* = \pi \rho_c c_c k_c (\Delta T_s)^2 / 4 \dot{q} \quad (2.37)$$

yields the required relationship

$$q^*/q_{ss} = (\pi/4)(1 - Q_m / c_c \Delta T_s) \quad (2.38)$$

The principal limiting assumptions are that the surface temperature is the same for onset of pyrolysis as for steady-state burning independent of heating rate, and that heat effects at the surface can be represented by a constant Q_m . In Ref. 51, the constant temperature assumption was made but Q_m was taken as zero in arriving at the conclusion that the heat added, up to the onset of pyrolysis, equalled the excess enthalpy for steady-state. The error of this assumption is evident from an inspection of Eq. 2.38 even when $Q_m = 0$.

2.2. HEATING OF A REACTIVE, OPAQUE SOLID, WITH STATIONARY BOUNDARY, NEGLECTING EFFECT OF REACTANT DEPLETION

A common feature of all solid phase thermal theories which include chemical reactivity is the occurrence of a temperature-dependent heat generation term in the field equation (Ref. 3, 15, 16, 21, 23, 28, 42, and 43) and/or in the boundary condition (Ref. 9, 37). The term is of the exponential Arrhenius type, so that as the solid is heated, the rate of heat generation increases, leading to even higher temperatures. Eventually, a precipitous rise in temperature occurs as the chemical term becomes dominant over the external heat input and loss terms. No longer is it necessary to draw upon the artificial concept of an ignition temperature, since the solid propellant contains within itself the attribute of self-heating, and the behavior of the model may be studied to determine ignition conditions. As noted in the introduction, this study is complicated by problems of definition of "ignition."

The nonlinearity introduced by including the chemical heating term precludes the rigorous analytical solution of the problem, necessitating numerical procedures. Some reduction in complexity is afforded by neglecting boundary motion, absorption of radiant energy in depth, and the effect of depletion of reactants on the reaction rate. Nevertheless, the number of cases treated is fewer than for the inert model. The cases to be discussed differ only in the mode of heat transfer imposed at the stationary boundary.

2.2.1. Constant Surface Temperature With No Film Drop.

As previously discussed in section 2.1.1.1., the results of hot-plate experiments do not substantiate the theory of critical ignition temperature because of variation of ignition delay (t^*) with block temperature. Only partial qualitative explanation of this variation is afforded by consideration of a gas film drop.

It is of interest in this connection to consider the characteristics of a model in which a solid phase chemical reaction is included for the case of constant surface temperature, such as would be realized by bringing a propellant sample into contact with a metal block of high thermal responsivity ($\sqrt{k\rho c}$). Analyses have been carried out (Ref. 3 and 21) in which the choice of ignition criterion constitutes the only distinction. The equations considered were

$$\rho_c c_c (\partial T / \partial t) = k_c (\partial^2 T / \partial x^2) + B_c \exp(-E_c / RT) \quad (2.39)$$

$$T = T_i \quad \text{at } t = 0 \quad (2.40)$$

$$T = T_{\infty} \equiv T_i \quad \text{at } x = \infty \quad (2.41)$$

$$T = T_s > T_i \quad \text{at } x = 0 \quad (2.42)$$

The boundary condition expressed by Eq. 2.41 is not strictly correct since the presence of the reactive term in Eq. 2.39 precludes a constant temperature anywhere within the solid. However, this condition is sufficiently accurate for short times. In Ref. 21, the equations were solved numerically, ignition being somewhat indefinitely defined by a rapid increase in temperature near the surface ($x = 0$). The surface temperature clearly cannot rise because it is being held at T_s (Eq. 2.42). Ignition is considered as occurring in Ref. 3 when the (decreasing) heat flux per unit area of propellant surface is just equal to the total (increasing) rate of chemical heat generation beneath the surface. In either case, the results may be summarized by the following empirical equation:

$$\log_e t^* = b_1/T_s + b_2 \quad (2.43)$$

where b_1 is approximately equal to E_c/R and b_2 is dependent (in a different functional manner for each cited reference) upon the thermal and kinetic properties and the initial and surface temperatures. Experimental agreement with the analyses is found in Ref. 54, where a straight line relationship is presented correlating $\log_e t^*$ and $1/T_s$.

2.2.2. Constant Gas Temperature and Constant Film Coefficient.

The paper by Hicks (Ref. 28) represents one of the earliest published efforts for which both time and space dependence of temperature were retained in the mathematical treatment of the ignition of a chemically reactive solid. The equations which were solved numerically are

$$\rho_c c_c (\partial T / \partial t) = k_c (\partial^2 T / \partial x^2) + B_c \exp(-E_c/RT) \quad (2.44)$$

$$-k_c (\partial T / \partial x) = H(T_g - T) \quad \text{at } x = 0 \quad (2.45)$$

$$(\partial T / \partial x) = 0 \quad \text{at } x = \infty \quad (2.46)$$

$$T = T_i \quad \text{at } t = 0 \quad (2.47)$$

$$T_g = T_{g1} \quad \text{for } 0 < t < t_h \quad (2.48)$$

$$T_g = T_{g2} \quad \text{for } t_h < t ; T_{g2} < T_{g1} \quad (2.49)$$

It is seen that the model consists of a semi-infinite solid in which depletion of reactants is neglected. The igniting stimulus is a hot gas at temperature T_{g1} from which heat flows for the time interval t_h .

Afterward, the surrounding gas temperature is discontinuously decreased to a low value T_{g2} , simulating cessation of the igniter output. The ignition event is said to have occurred at a time when the surface temperature reaches a value $T_s = 0.045E_c/R$. This is not equivalent to choosing a critical ignition temperature, but merely assures that, in the present case, the temperature is rising precipitously. It is shown that the exact choice of the ignition criterion does not significantly affect the results. Reference to Fig. 2.4 will facilitate understanding of the terms used to describe the following principal features of the results.

For reference purposes, an adiabatic ignition time t^* is defined as the time required for a solid of uniform temperature to reach the temperature $T_s = 0.045E_c/R$ with no external heating. Owing to the adiabatic assumption and the neglect of depletion of reactants, ignition according to this criterion will always occur. The minimum ignition time, t_{min}^* , is the time required for ignition if heating is continued until the ignition criterion is satisfied. As the heating time, t_h , is decreased slightly from this value, the ignition time, t^* , increases very rapidly until the critical heating time, t_{cr} , is reached for which the ignition time is just equal to t_{cr}^* . If t_h is decreased below t_{cr} , the ignition time, based on surface temperature, exceeds t_{cr}^* , owing to the feature of the model which permits surface cooling after shutoff of ignition. In such cases, the ignition criterion will be satisfied at some location beneath the surface at a time less than t_{cr}^* . The principal results of Hicks's work are formulated in terms of t_{min}^* and t_{cr}^* and in empirical methods for estimating these quantities without solving the differential equation. Figure 2.5 shows the effect of pertinent parameters upon the minimum ignition time. It should be remembered that the method of heating does not lead exactly to constant \dot{q} ; nevertheless the product $h \theta_{g1}$ may be considered as a reasonably accurate measure of \dot{q} when the

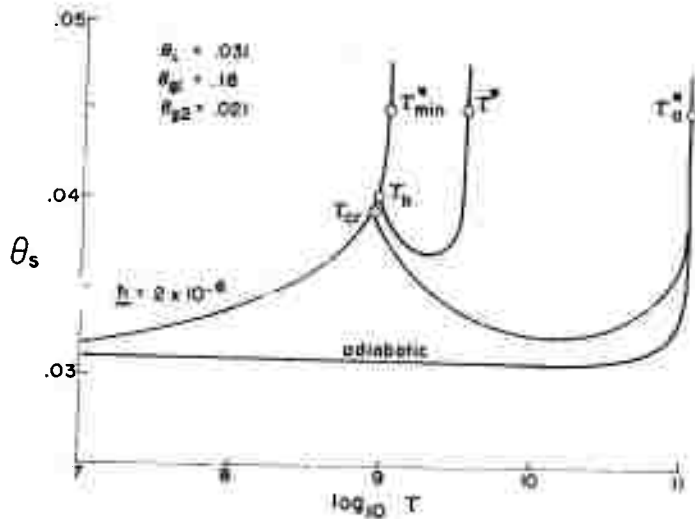


FIG. 2.4. Reduced Plot of Surface Temperature vs. Time for Selected Values of Parameters in Hicks's Theory (Ref. 28).

propellant surface temperature does not rise appreciably compared to T_{g1} . Salient points of Fig. 2.5 are that the value of τ_{\min}^* is nearly independent of θ_{g1} for low heating rates and high initial propellant temperature T_1 , while for low initial temperature and moderate to high heating rates, the heating rate is controlling. The physical interpretation of these observations involves the recognition of the relative importance of heating by external flux and by internal chemical reaction. For high external flux compared to chemical heating, the minimum ignition time would be controlled by external heating in a manner approaching that of an inert solid. The lower the initial temperature, the greater would be the range over which the external heating dominates. This tendency is illustrated by the upper curves in Fig. 2.5. On the other hand, at higher initial temperatures, the chemical heating becomes dominant over external heating for a wider range of values of external heating. Hence, the

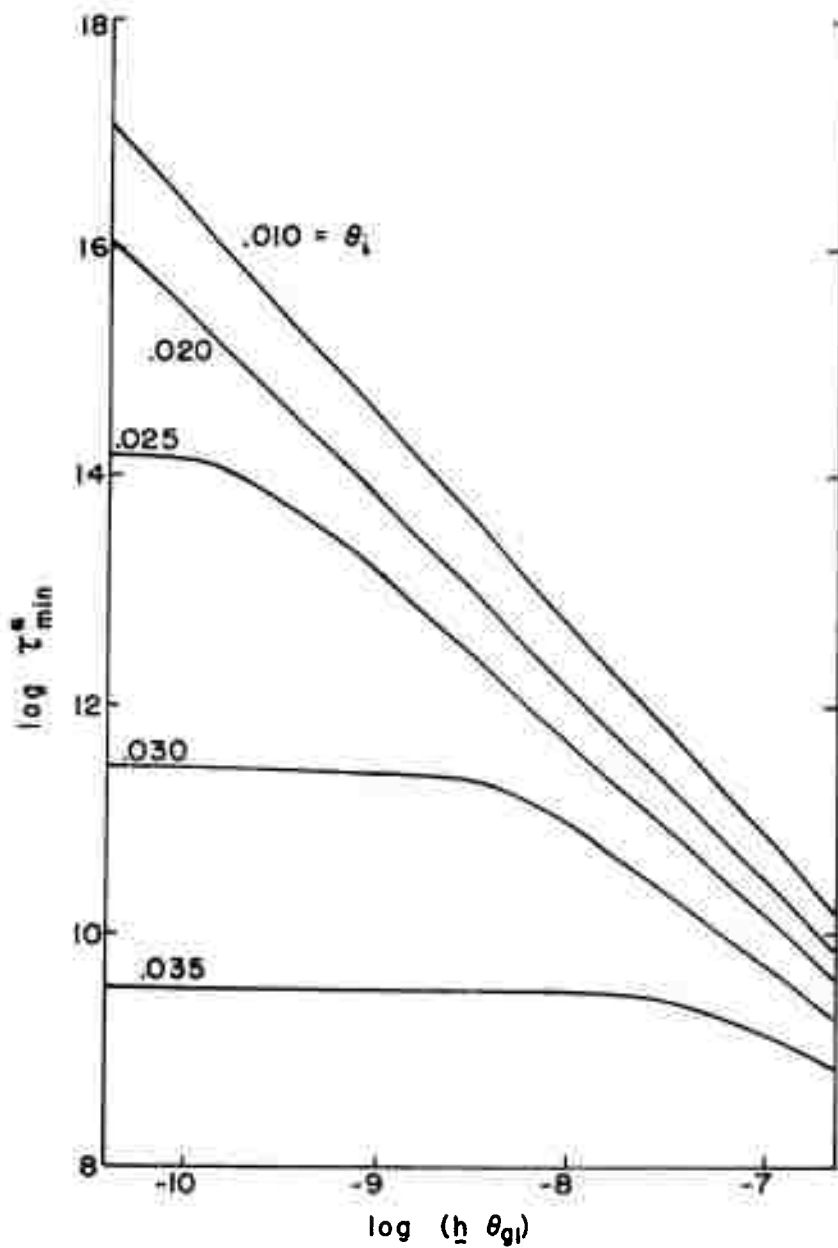


FIG. 2.5. Reduced Plot of Minimum Ignition Time vs. Initial Heating Rate for Selected Values of Parameters in Hicks's Theory (Ref. 28).

amount of external heating under these conditions has little effect on minimum ignition time, a result illustrated by the horizontal portions of the curves of Fig. 2.5. The effect of the kinetic constants is not so easily described because of the presence of the quantities B_c and E_c in the coordinate scales and the parameter. It is noteworthy that the slope of the curves in Fig. 2.5, even in the straight portions, is significantly less in magnitude than 2 (corresponding to 1 on a $\log q$ vs. $\log \dot{q}$ plot), a feature evident also in more recent investigations. The theory also predicts the effect of shutoff of the igniting source, viz., that the higher the heating rate, the higher must be the surface temperature at shutoff in order for ignition to be achieved. The physical explanation of this phenomenon is that at higher heating rates, a thinner layer of material is raised to a temperature sufficient to assure significant chemical reaction, while at the same time a steeper thermal gradient is set up to conduct away the heat generated. This aspect of the model was discussed in the introduction and is in agreement with results of later investigations (Ref. 3, 9, 37, 42, and 43) and experiments, especially on double-base propellants.

2.2.3. Constant Radiant Flux.

Nearly all theoretical investigations on heating of reactive solids have used the boundary condition of constant radiant flux. This choice is dictated partly by the reduction in number of parameters required to characterize the solutions and partly by the desire to compare results with experimental data obtained from arc-image apparatus. The case of variable radiant flux was considered (Ref. 15 and 16) in connection with initiation of high explosives by very short, high intensity radiation pulses but the area of investigation and results reported there is not applicable to ignition of solid propellants.

The heating of a reactive solid by constant radiant flux has been explored mathematically for two general cases. In one, the reactivity was considered to be concentrated at the surface and/or in bulk while in the other, only bulk reactions are considered.

2.2.3.1. Surface Reaction. In Ref. 37, the equations were solved in which the chemical heating term was included not only in Eq. 2.1 but in Eq. 2.3 as part of a boundary condition containing a constant flux and two chemical heating terms of the Arrhenius type, one endothermic and one exothermic.⁴ In Ref. 9, the model of Ref. 37 is

⁴ The physical meaning of this model is not clear since the effect of surface regression was neglected. This is inconsistent with a surface reaction model since no finite reaction rate is possible without surface regression.

simplified by eliminating the bulk heating term and the endothermic surface heating term. The bulk term was not considered because it was felt that the main part of the reaction was concentrated at the surface. Regarding the endothermic term, it was argued from results of Ref. 37 that either (1) the relative activation energies of real simultaneous endothermic and exothermic reactions are not such that the former is important or (2) that an endothermic reaction followed by an exothermic reaction is representable by a single effective exothermic reaction. The equations solved are

$$\rho_c c_c (\partial T / \partial t) = k_c (\partial^2 T / \partial x^2) \quad (2.50)$$

$$-k_c (\partial T / \partial x) = \dot{q} + B_s \exp(-E_s / RT) \quad \text{at } x = 0 \quad (2.51)$$

$$T = T_\infty \equiv T_i \quad \text{at } x = \infty \quad (2.52)$$

$$T = T_i \quad \text{at } t = 0 \quad (2.53)$$

In writing Eq. 2.51, the retention of the surface heating term in the absence of surface regression may be interpreted physically as heat originating from a gas phase or heterogeneous reaction with no consumption of the solid phase. Ignition was defined as when the chemical term exceeded the \dot{q} term and was changing rapidly with time. Results of the computation can be summarized as follows:

(1) The square roots of calculated ignition time $\sqrt{t^*}$ are roughly proportional to $1/\dot{q}$. When $\log \sqrt{t^*}$ is plotted vs. $\log \dot{q}$, nearly straight lines are obtained with having a slope

$$S = 4.2 RT_i / E_c - 1 \quad (2.54)$$

Equation 2.54 may be applied to experimental data to obtain activation energies. However, S is normally close to minus one so that small errors in determining S can lead to large errors in E_c . It is mentioned that E_c may be calculated by applying Hicks's results to a plot of $\log \sqrt{t^*}$ vs. $1/\dot{q}$ and yields values of E_c approximately twice as great as obtained from Eq. 2.54.

(2) A surface temperature at ignition (T_{sl}^*) may be calculated from

$$T_{sl}^* = T_i + 2\dot{q} \sqrt{t^* / \pi k_c \rho_c c_c} \quad (2.55)$$

Equation 2.55 is the solution of Eq. 2.50-2.53 ignoring the chemical reaction term in Eq. 2.51. The value of t^* , however, is the ignition time determined by numerically solving the equations including chemical reactivity. The value of T_{sl}^* so calculated is found to be nearly independent of T_i .

- (3) The ignition time is found by computer results to be given by

$$\sqrt{t^*} = (\sqrt{\pi k_c \rho_c c_c / 2 \dot{q}}) \{ (E_g/R) / [1 - 1.04 \log_e (\dot{q}/B_g)] - T_i \} \quad (2.56)$$

An obvious breakdown of Eq. 2.56 occurs when the denominator in the bracketed term becomes zero.

- (4) Regarding the effect of shutting off the flux the following results were found:

(a) If $B_g \exp(-E_g/RT_g) \leq \dot{q}$ at the time of shutoff, ignition did not occur until a period of from ten to 20 times the initial heating period.

(b) The difference in ignition times for pulsed and continuous flux application is only 1-2 percent of the ignition time for continuous application of external flux. Hence, it would seem that ignition experiments in which external heating is continuous until ignition would give similar results to experiments in which the external flux is discontinued at just the minimum ignition time (comparable to t_{min}^* in Hicks's theory). It is mentioned in Ref. 37 that the equivalence of pulsed and continuous experiments would be invalidated in case combustible gases were evolved during the pulsed period and subsequently ignited spontaneously to provide sufficient energy feedback to complete the ignition process. An example given was the case of arc-image experiments involving small pre-pressurized test chambers.

2.2.3.2. Bulk Reaction. In Ref. 43 solutions were presented for a solid-phase thermal model similar to Hicks's. The only differences were in the use of a constant flux boundary condition during heating and an insulated boundary after heating was shut off. Results of the computations are displayed for typical values of parameters in Fig. 2.6 and 2.7. In Fig. 2.6, the increase in surface temperature is shown as a function of the product of $q\dot{q}$ which for a given \dot{q} is proportional to time. The lower curve is the solution for no chemical heating while the curves for various values of \dot{q} indicate that the surface temperature at which the runaway chemical reaction (vertical section of constant \dot{q} curves) occurs is increased significantly at the higher heating rates. A qualitative argument, first presented in Ref. 42 and reproduced at the end of section 2.2.2, affords a reasonable explanation of this result. A quantitative extension of the argument predicts an effect of \dot{q} upon surface temperature for runaway reaction which is in excellent agreement with the results of calculations from Ref. 17. In Fig. 2.7 the results (isotherms) are shown on the conventional $\log q$ vs. $\log \dot{q}$ plot. It is seen that (1) the constant surface temperature curves all approach an upper asymptote, derived from

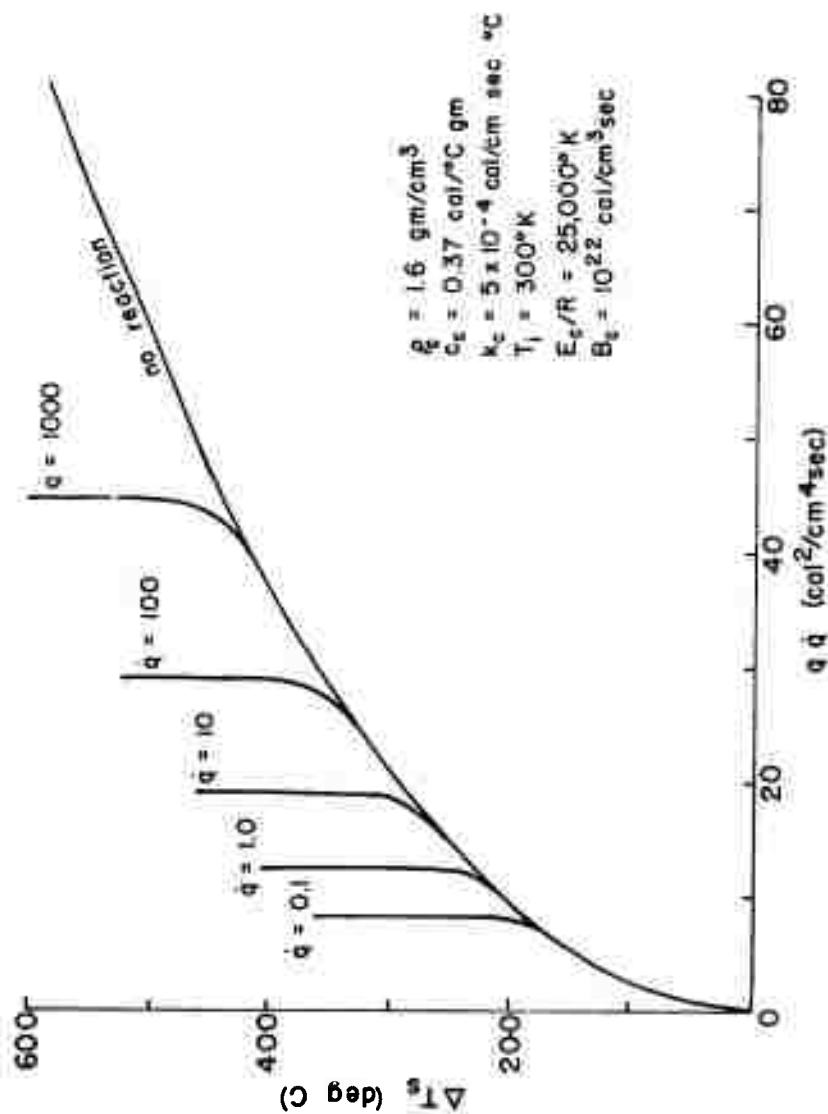


FIG. 2.6. Typical Correlation of Calculated Surface Temperature Rise as a Function of q and \dot{q} for Reactive Solids in Condensed-Phase (Thermal) Theory.

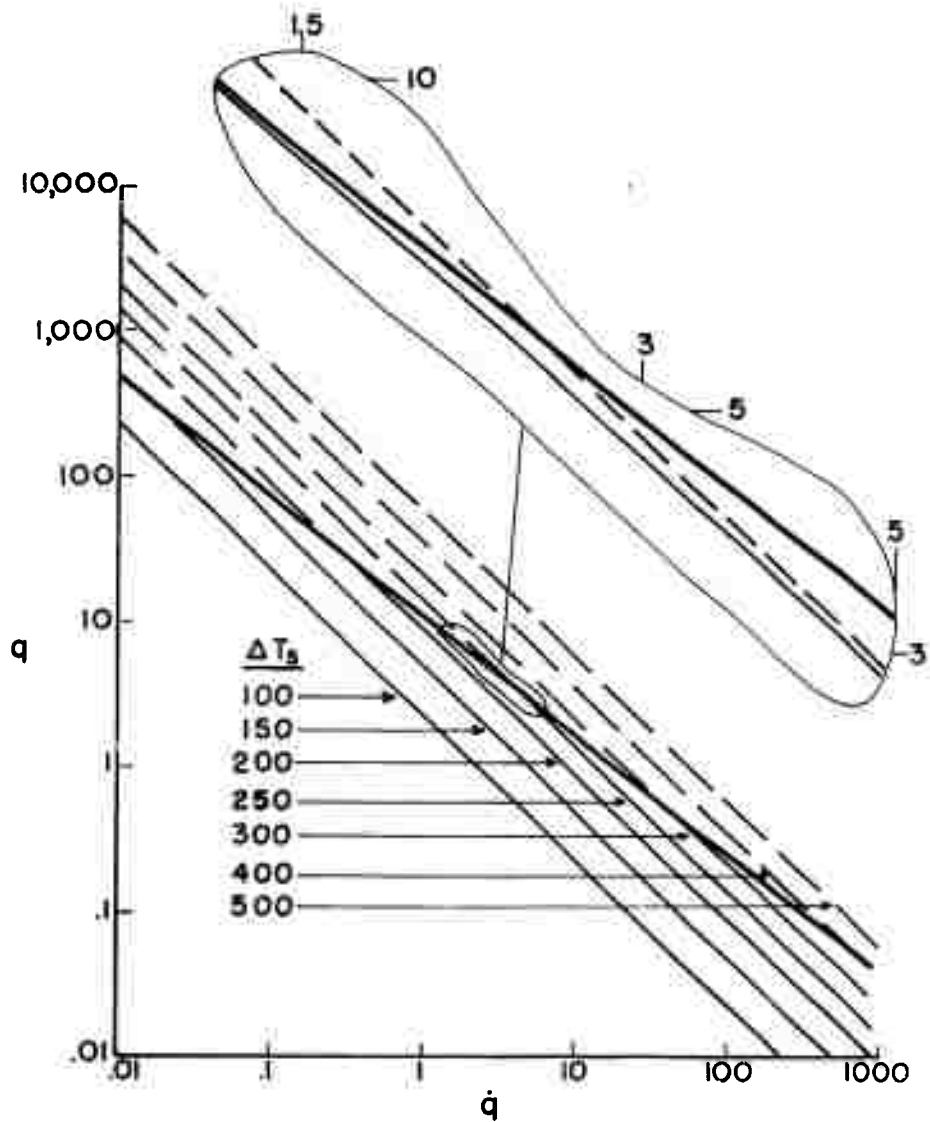


FIG. 2.7. Constant Surface Temperature Lines for Condensed-Phase Theory. (Light solid lines are T_s for chemically reactive solid; dashed lines are T_s for chemically inert solid. Heavy solid line indicates region of convergence of surface isotherms for the reactive case. Parameters as in Fig. 2.6).

a consideration of the near vertical sections of the constant \dot{q} curves of Fig. 2.6; (2) the constant temperature curves are identical to those for no chemical heating until close approach to the asymptote; and (3) at higher heating rates, the asymptote represents a region of convergence of curves of higher constant surface temperature. (These results were discussed also in the introduction, and provided the data for Fig. 1.2). Even though the asymptote appears nearly straight, there are combinations of the parameters E_c/R and B_c for which there is a perceptible curvature (see Fig. 2.8). Upon comparison of the limiting asymptotes for different values of the kinetic parameters E_c and B_c , it is found that:

(1) For a constant value of B_c , an increase in activation energy, E_c , has the following results:

(a) A higher energy, q , and surface temperature, T_s , are required to produce runaway conditions.

(b) The slope of the limit line on a $\log q$ vs. $\log \dot{q}$ plot is steeper, indicating that the total heat required for runaway conditions is more dependent upon heating rate.

(2) For a constant value of E_c , an increase in B_c (product of heat of explosion and frequency factor) has the following results:

(a) A lower energy, q , and surface temperature, T_s , are required to produce runaway conditions.

(b) The slope of the limit line on a $\log q$ vs. $\log \dot{q}$ plot is less steep, indicating that the total heat required for runaway conditions is less dependent upon heating rate.

The effect of shutoff of the external heating was investigated and it was found that if the surface temperature rise at shutoff had reached approximately 1.15 times the surface temperature rise with no chemical heating, the runaway occurred very rapidly after shutoff of heating. This ratio, 1.15, was determined numerically for only one set of parameters and used subsequently as a criterion of ignition for other cases.

In all solid-phase thermal theories applicable to propellant ignition, the effect of depletion of reactants has been neglected. An estimate of the extent of depletion was made (Ref. 17, 43) by computing the time integral of the reaction rate at the surface and hence of the degree of surface reaction. For realistic values of \dot{q} , Q_c , B_c , and E_c , it was found that around 20 percent of the reactant was consumed, which is great enough to justify further study.

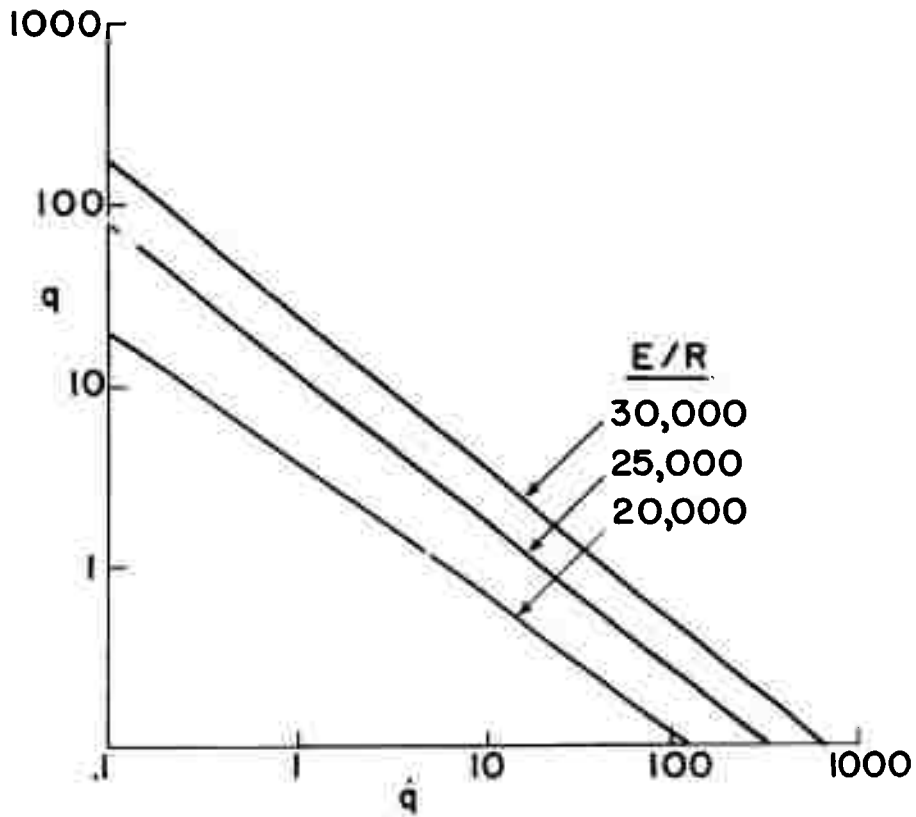


FIG. 2.8. Limiting Asymptotes for Condensed-Phase Theory With Bulk Chemical Reaction. $B_c = 10^{22}$ cal/cm³ sec. Other parameters as in Fig. 2.6.

2.3. HEATING OF A REACTIVE SOLID WITH STATIONARY BOUNDARY, CONSIDERING THE EFFECT OF REACTANT DEPLETION

Comprehensive studies of the effect of reactant depletion have been limited almost exclusively to cases in which the time or space variation of temperature has been ignored (Ref. 1, 47, 49, and 50). While of interest in the investigation of critical geometries or induction periods for which the assumption of time or space uniformity of temperature is a valid approximation, the results can scarcely be applied to solid propellant ignition involving propagation of thermal waves. Several specialized numerical analyses have been made in which both the time and space variation of temperature were considered (Ref. 11, 22, 46, and 52). Results are of limited utility in propellant work because of the primitive nature of the computers used (Ref. 11 and 22) and uncertainties of the solutions or because of motivation of the study toward wood burning with a limited range of parameters (Ref. 46 and 52).

Recent efforts include a joint program by NCTS and Stanford Research Institute (SRI), in which IBM calculations were made to determine the effect of depletion of reactants and of absorption of radiant energy in depth (Ref. 18 and 19). Reduction of the data to manageable form has not yet been completed.

3. HYPERGOLIC AND HETEROGENEOUS IGNITION THEORIES

Because of the vulnerability of propellant binder materials to surface attack by oxidizing gases, consideration has been given to the possibility that this surface reaction might be the controlling exothermic step in ignition. This concept was exploited by Allen and Pinns (Ref. 2), who studied ignition induced by exposure of propellants and their ingredients to atmospheres of room-temperature chlorine trifluoride. Their test results showed that all three propellant ingredients (binder, ammonium perchlorate (AP) powder, and aluminum powder) ignited spontaneously in gaseous ClF_3 . Ignition delay increased as ClF_3 pressure was reduced, progressing to a low pressure limit below which ignition did not occur (Fig. 3.1a and 3.1b). Addition of either metal or AP powder to the binder generally increased the ignition delay (Fig. 3.1c and 3.1d), although a mix of 30 percent AP, 70 percent polyurethane binder was easier to ignite than pure polyurethane at low pressure. Addition of aluminum in normal proportions to the propellant aided ignition (Fig. 3.1e). These results establish the relevance of a hypergolic mechanism for the case of ClF_3 , and raise the question of possible similar behavior of weaker oxidizers at the higher temperatures encountered during ignition by external heating. The results also suggest that the relevant reactions may not be restricted to atmospheric attack on binder. It should be noted that the ignition delays were based on the presumption that ignition is concurrent with the onset of

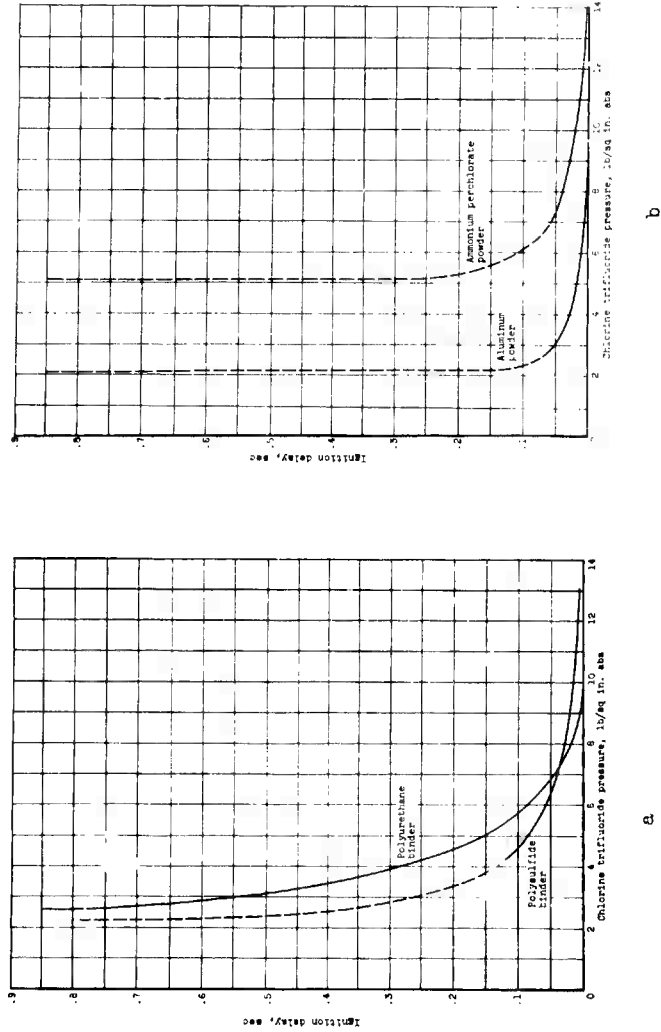
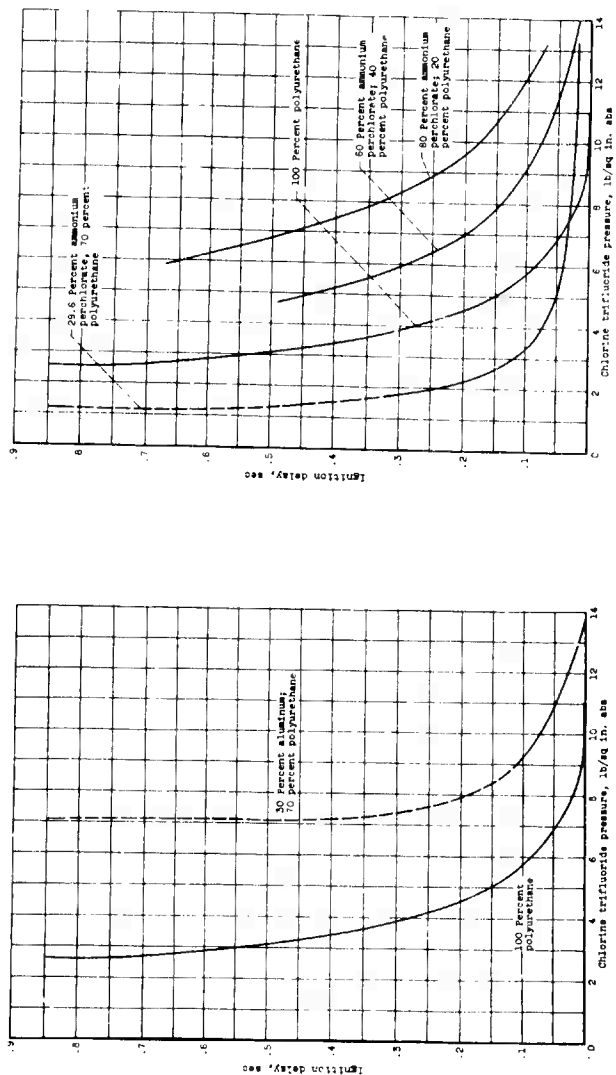


FIG. 3.1a and 3.1b. Dependency of Ignition Delay Time of Propellant and Propellant Constituents on Hypergolic Oxidizer Concentration (From Ref. 2).



c

d

FIG. 3.1c and 3.1d. Dependency of Ignition Delay Time of Propellant and Propellant Constituents on Hypergolic Oxidizer Concentration (From Ref. 2).

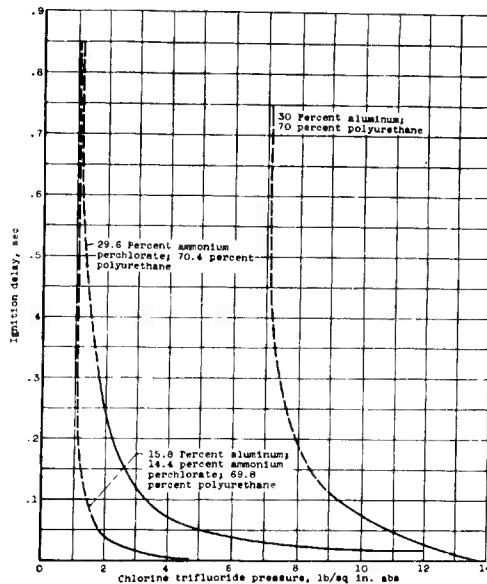


FIG. 3.1e. Dependency of Ignition Delay Time of Propellant and Propellant Constituents on Hypergolic Oxidizer Concentration (From Ref. 2).

luminous combustion, a presumption that may not be consistent over the range of composition considered.

Further support of a hypergolic ignition mechanism was provided in work of Anderson and Brown (Ref. 5), who studied the effect of oxidizer fraction and pressure on ignition delay using ClF_3 and F_2 with binders and propellants. This experimental work was accompanied by study of an analytical model which permitted calculation of ignition delay times. This "hypergolic" ignition theory represented the problem as one-dimensional, with the propellant as a semi-infinite slab of fuel and the oxidizer as an adjoining semi-infinite volume of oxidizer. The exothermic reaction was assumed to be localized at the interface, and the reaction rate was presumed to be controlled by temperature and by diffusion of oxidizer to the surface from the gas field. In later work the role of heat from non-chemical sources was apparently considered (Ref. 7, 14), but details are lacking.

The role of the solid oxidizer component of the propellant in hypergolic ignition has been explored qualitatively (Ref. 7); in the limiting case where the solid oxidizer is the sole source of oxidizing species, the theory is referred to as the "heterogeneous ignition theory." Because of the geometrical complexity of the propellant microstructure, the heterogeneous theory has remained qualitative.

3.1. HYPERGOLIC IGNITION

In hypergolic ignition (Ref. 5) the oxidizer and binder are brought into contact, and exothermic reactions start spontaneously at room temperature. Because of the exponential dependence of reaction rate on temperature, an approximately exponential temperature rise occurs until the reactant concentration drops off due to limited diffusion rates and consumption of initial reactants. In the analysis it is concluded that extremely high rates of surface temperature rise may occur before diffusion becomes limiting, and the temperatures may be far in excess of those required for the propellant to sustain burning with its own oxidizer. Accordingly, ignition is defined in terms of attainment of some judiciously chosen temperature rise rate or surface temperature, thereby circumventing the difficulties associated with the emergence of a diffusion-limited situation and the absence of any well defined steady-state solution to the hypergolic model. It must be presumed that this procedure will break down at low oxidizer concentrations or with low energy oxidizer-fuel reactions, where diffusion rates will be important before decisive temperature rises will occur. Because of the possible importance of diffusion, the subject was examined further by one of the present authors and is reported in the Appendix.

3.1.1. Hypergolic Ignition Model.

The hypergolic ignition model of Anderson and Brown (Ref. 5) is shown pictorially in Fig. 3.2. The model which considers the gas phase and the condensed phase as semi-infinite regions with constant properties (other than concentration and temperature) is described mathematically by Eq. 3.1-3.16 inclusive.

$$(\partial T_c / \partial t) = \alpha_c (\partial^2 T_c / \partial x^2) \quad (3.1)$$

$$(\partial T_g / \partial t) = \alpha_g (\partial^2 T_g / \partial x^2) \quad (3.2)$$

$$(\partial C_o / \partial t) = D_o (\partial^2 C_o / \partial x^2) \quad (3.3)$$

$$(\partial C_p / \partial t) = D_p (\partial^2 C_p / \partial x^2) \quad (3.4)$$

$$T_c(x, 0) = T_i \quad (3.5)$$

$$T_g(x, 0) = T_i \quad (3.6)$$

$$C_o(x, 0) = C_{oi} \quad (3.7)$$

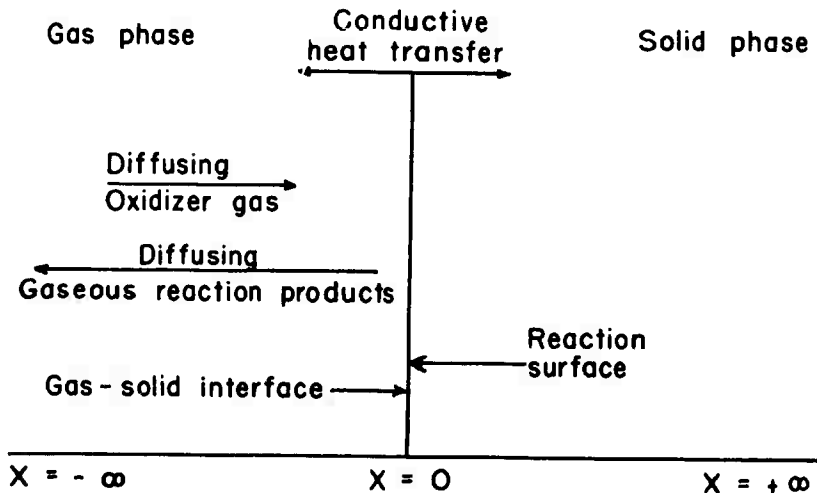


FIG. 3.2. Hypergolic Ignition Model.

$$C_p(x,0) = 0 \quad (3.8)$$

$$T_c(\infty, t) = T_i \quad (3.9)$$

$$T_s(-\infty, t) = T_i \quad (3.10)$$

$$C_o(-\infty, t) = C_{oi} \quad (3.11)$$

$$C_p(-\infty, t) = 0 \quad (3.12)$$

$$T_g = T_c = T_s \quad \text{at } x = 0 \quad (3.13)$$

$$D_p (\partial C_p / \partial x) = -\psi D_o (\partial C_o / \partial x) \quad \text{at } x = 0 \quad (3.14)$$

$$-D_o Q_s (\partial C_o / \partial x) = -k_c (\partial T_c / \partial x) + k_g (\partial T_g / \partial x) + \quad (3.15)$$

$$c_p (T - T_i) D_p (\partial C_p / \partial x) + c_o (T - T_i) D_o (\partial C_o / \partial x) \quad \text{at } x = 0$$

$$-D_o(\partial C_o/\partial x) = C_o^a Z_{exp}(-E/RT) \quad \text{at } x = 0 \quad (3.16)$$

Equations 3.1-3.4 describe the diffusion of heat and oxidizer, and reaction products. No convection, regression of the surface, or accumulation of condensed phase non-reactants or products at the surface are considered. Equations 3.5-3.8 are the four required initial conditions and Eq. 3.8-3.12 are the boundary conditions applicable to the assumed semi-infinite model. The final four-boundary conditions all apply to conditions at the solid-gas phase interface. Equation 3.13 indicates a temperature equality of the two phases at the interface. Equation 3.14 indicates that all of the oxidizer that diffuses to the surface reacts to form products which in turn diffuse from the surface. The original expression in Ref. 6 for the heat balance at the propellant surface included the last two terms of Eq. 3.15. An assumption of a Lewis number of one was made and the original boundary condition, as well as the field equations involving temperature, were expressed in terms of enthalpy rather than temperature. When written in this form no separate terms involving sensible heat transport appeared in the boundary equation. The mathematical model is presented in this form in Ref. 5.

In any event the effect of assuming a stationary boundary, a constant Q_s , and a Lewis number of one appears to be of the same magnitude as the sensible heat transport terms in Eq. 3.15. A computation showed that the algebraic sum of the last two terms in Eq. 3.15 is of the order of one percent of the term on the left side of the equation. In the Appendix, Eq. 3.15, minus the sensible heat transport terms, was used as the surface heat balance boundary condition. The final boundary condition equates the rate of surface reaction of the oxidizer to the rate of diffusion of oxidizer to the surface.

Because of the nonlinearity arising from Eq. 3.16, solutions to the family of equations were obtained (Ref. 5) with a high speed computer. Some analytical solutions of special cases not previously reported are presented in the Appendix.

3.1.2. Assumptions of the Hypergolic Model.

The following assumptions regarding the model were listed in Ref. 5.

(1) The diffusion of heat and mass can be represented by the concept of one-dimensional, semi-infinite slabs.

(2) Thermodynamic and transport properties are independent of temperature. Gas properties are taken to be at their values at initial conditions.

(3) The chemical heating starts instantaneously upon hypergolic oxidizer-propellant contact.

(4) The heterogeneous chemical reaction between the gaseous oxidizer and the solid propellant for the simplest case is first order with respect to gaseous hypergolic oxidizer concentration and zero order with respect to the exposed solid fuel.

(5) The reaction rate is a function of temperature as described by an Arrhenius type relation.

(6) Heat loss from the reaction surface into the stagnant oxidizer gas and the solid propellant phase is by pure conduction and by natural convection⁵ of the diffusing species.

(7) Heat is generated only as a result of reaction between the gaseous oxidizer and the exposed fuel of the solid.

(8) The total heat of reaction is released at the propellant surface.

(9) The gaseous layer and the fuel surface at the reaction interface are always at thermal equilibrium.

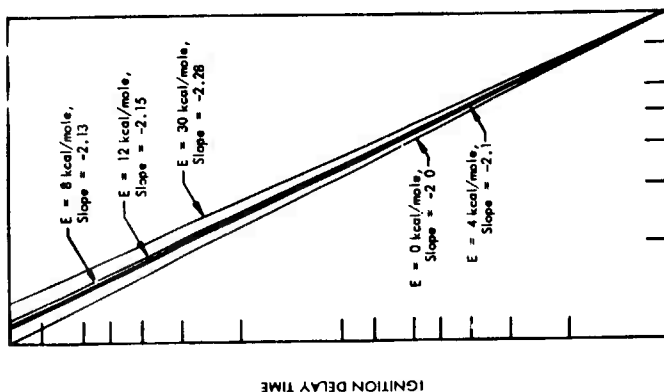
(10) The fuel substrate or solid propellant is isotropic and remains so.

As noted earlier, this model also makes the commonly used assumptions that there is no bulk convective flow of gas at the surface and any receding of the solid surface may be neglected. It is assumed that an effective overall Arrhenius type expression can be used to describe the combined effects of chemical kinetics and surface absorption phenomena.

3.1.3. Mathematical Solution of Hypergolic Model.

Analytical solution of the mathematical model was judged to be impractical, and the problem was coded and run on a digital computer (Ref. 5). No details regarding the computer program have been reported, and the full set of combinations of parameter values covered in the program is also unreported. Sample data are presented primarily in the form of graphs of log ignition time versus log oxidizer concentration, referred to in the following as t^* vs. C_{O_i} curves, with curves selected to show the effect of kinetic and physical constants of the system. Particular attention is directed to the trends of these curves, since independently determined values of the kinetic parameters were not available for estimates of the actual value of ignition delay. Slope of the t^* vs. C_{O_i} curves was found to be rather sensitive to order of reaction, only mildly sensitive to activation energy, and independent of the pre-exponential factor, heat of reaction and thermal conductivity (Fig. 3.3-3.7).

⁵It is presumed that the author means mass transport by diffusion.



HYPERGOL CONCENTRATION

FIG. 3.4. Effect of Activation Energy on the Slope of Log t^* Versus Log C_{oi} (From Ref. 5).

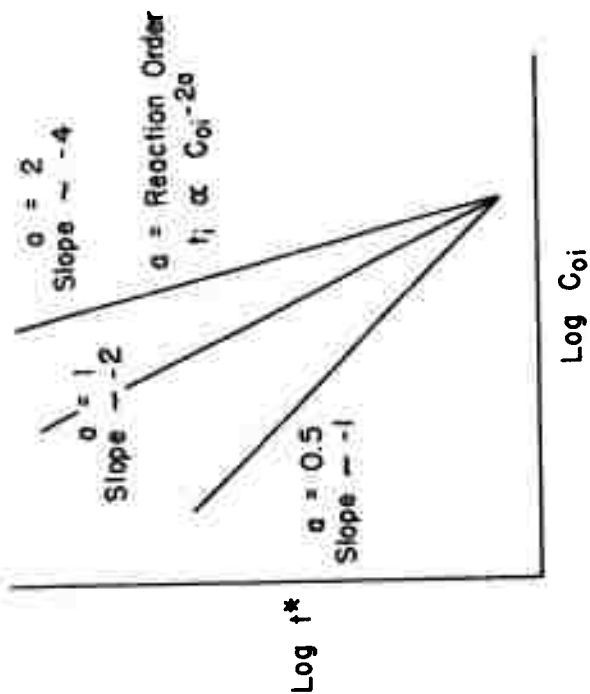


FIG. 3.3. Effect of Reaction Order on the Slope of Log t^* Versus Log C_{oi} (From Ref. 5).

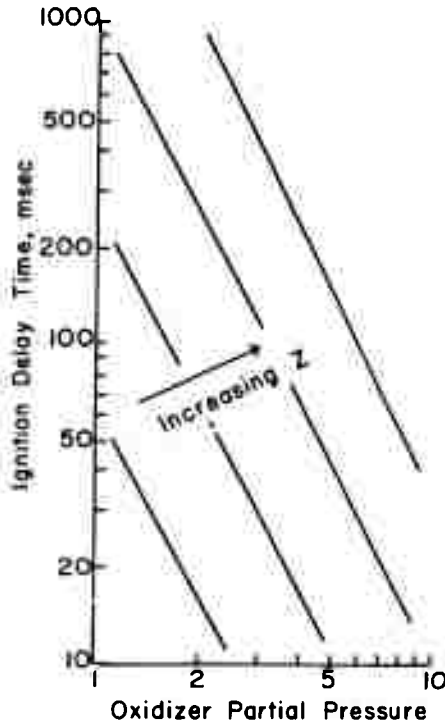


FIG. 3.5. Effect of Pre-Exponential Factor on the Slope of $\log t^*$ Versus $\log C_{O_1}$ (From Ref. 5). (It is felt that the arrow should be pointing in the opposite direction.)

Comparison of experiment and theory (Ref. 5) was made by adjustment of parameters. In this adjustment, the order of reaction was assumed to be one (because it gave a relatively good fit of slope and seemed appropriate on fundamental grounds), and the pre-exponential factor and activation energy were chosen in pairs of values satisfying one of a set of data points from experiment (the lower point in Fig. 3.8). The t^* vs. C_{O_1} curves corresponding to these $Z - E$ combinations were compared with the balance of the experimental data and an activation energy estimated on the basis of best fit (Fig. 3.9). The experiment was conducted with oxidizer concentration varied both by change in pressure and by constant-pressure dilution by nitrogen, with the ignition delays proving to be independent of the manner in which concentration was achieved. It is argued that

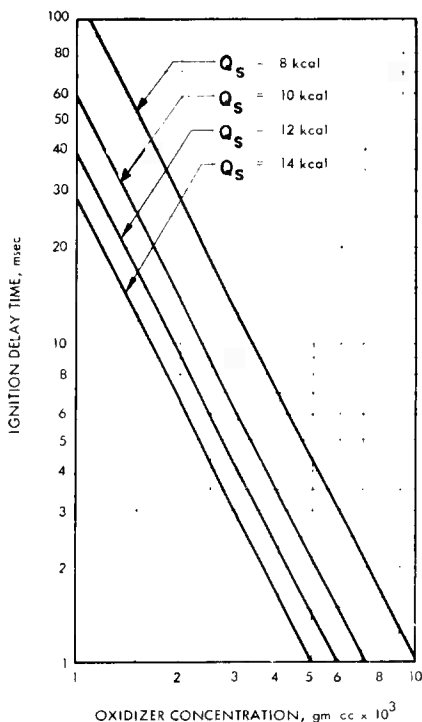


FIG. 3.6. Effect of Heat of Reaction on the Slope of $\log t^*$ Versus $\log C_{oi}$ (From Ref. 6).

this result establishes the dominance of reaction kinetics over diffusion in controlling ignition time.⁶ Experimental data from several

⁶ This is somewhat analogous to the condition in solid-phase theory that the ignition event be consummated before significant depletion of reactants. In both cases the condition is favored by high heats of reaction, high concentration of reactants, and low thermal responsivity ($\sqrt{k\rho c}$). In the hypergolic theory the assumption will presumably break down at low oxidizer concentration or with oxidizers having a low heat of reaction.

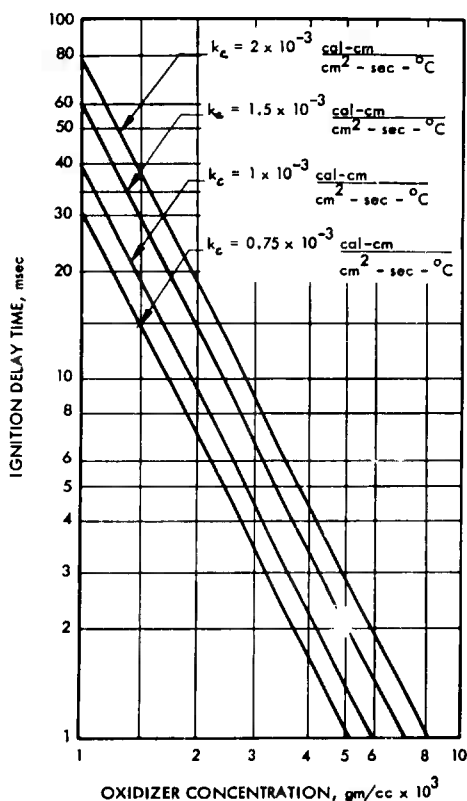


FIG. 3.7. Effect of Thermal Conductivity on the Slope of $\text{Log } t^*$ Versus $\text{Log } C_{oi}$ (From Ref. 6).

sources were fitted with theoretical curves by this method of adjustment of parameters, assuming in most cases that the order of reaction was one. Best fits were usually obtained with activation energies in the vicinity of 3-12 Kcal/mole.

The success in correlating experimental data with theory using plausible values of the kinetic parameters is cited as proof of the validity of the assumption of an exothermic heterogeneous reaction controlling ignition. The efforts to explain the experimental results on

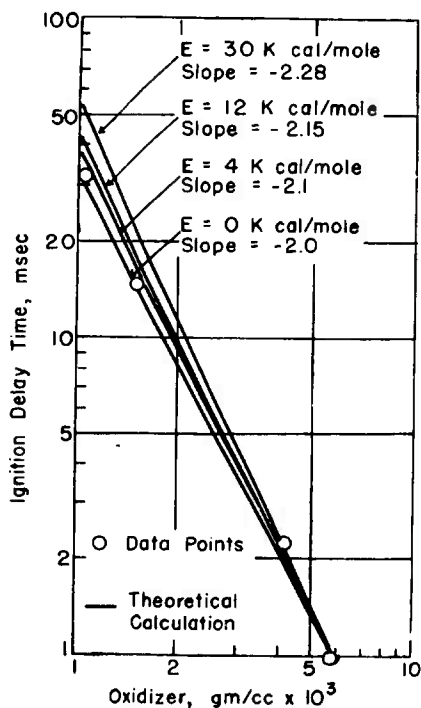


FIG. 3.8. Matching of Experimental and Calculated Ignition Data for PBAA/AN Composite Propellant by Adjustment of Parameters (From Ref. 6).

the basis of competitive theories are largely negative in character.

3.1.4. Discussion of the Hypergolic Ignition Theory.

The work reported in Ref. 5, 6, 14 constitutes a useful contribution to the literature on ignition, and seems to be effective in describing the ignition process for propellant fuel materials in atmospheres of powerful oxidizers. The relevance of the theory to propellants is less clearly established, but it appears that the heterogeneous

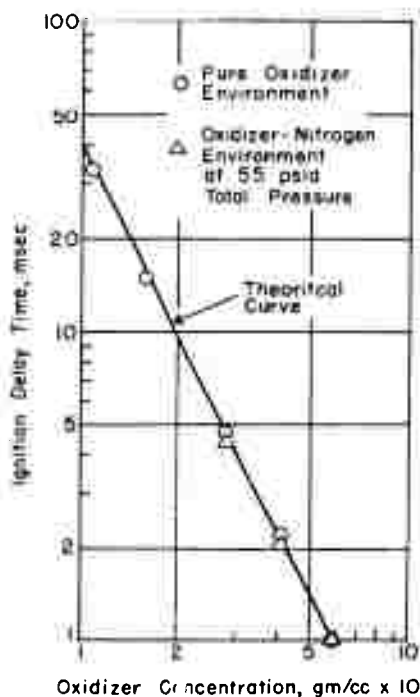


FIG. 3.9. Best Fit Agreement Between Experimental and Calculated Ignition Data for PBAA/AN Composite Propellant (From Ref. 6).

reaction between the gaseous oxidizers used and the propellant binder is still dominant in ignition. There are fundamental difficulties in definition of the attainment of ignition, since the hypergolic model does not have a steady-state solution and the transition to steady burning of a propellant necessarily involves the solid oxidizer decomposition and emergence of its products as the dominant oxidizing species for the fuel. The results to date suggest that hypergolic reactions are not displaced in ignition of real propellants until they have supplied enough energy to assure transition to "composite propellant burning", at least with ammonium perchlorate oxidizers.

There are a number of areas in which the treatment of the hypergolic theory could be improved. Thus, it would be helpful if the computer results were more fully reported, and the relevant parameters more fully detailed in the graphs. Some benefit would be realized by a more careful study of the analytical problem, including use of lumped variables and studies of analytical solutions of limiting cases to aid in physical insight and verification of computer results (see, for example, the Appendix). The analysis should be extended to include ignition in the

presence of external heat sources (such extension is discussed in Ref. 7 and 14, but apparently has not been carried out), in order to study the effect of oxidizing atmospheres that are not hypergolic at room temperature. Further study of the conditions under which diffusion controls the reaction rate would add greatly to perspective. It is not clear from reports to date that the computer program (Ref. 5) is coded to use the diffusion equations. If it is, the arguments regarding relative importance of diffusion and reaction kinetics would be greatly strengthened by support with computer results instead of vague references to a book (Ref. 5, 24). It seems likely that diffusion would become limiting over chemical kinetics in some cases of interest such as low absolute oxidizer concentration in the environmental gas.

3.2. HETEROGENEOUS IGNITION

In an attempt to elucidate the role of heterogeneous reactions in ignition of propellants in atmospheres that were either nonreactive or reactive only at elevated temperature, a qualitative theory has been evolved which considers the heterogeneous reaction between the propellant binder and the decomposition products of the solid oxidizer (Ref. 7 and 14).

3.2.1. Heterogeneous Ignition Model.

It is proposed in this theory that, following a thermal induction by external heating, the ammonium perchlorate oxidizer starts to decompose and provide hot oxidizer gas which attacks the fuel surface exothermally, providing the controlling runaway reaction. It is assumed that the oxidizer gas may emerge either at the exposed oxidizer surface or at oxidizer-binder interfaces near the surface. It is argued that at low pressures or with soft binders, the oxidizer gases accumulate in the region adjoining the outer propellant surface, and the time to ignition is dependent on the oxidizer gas concentration and pressure in a manner predicted by the hypergolic theory. At higher pressures or with more rigid binders, it is argued that the oxidizer gases liberated in the interfacial structure may be more effectively confined at these interfaces, and may reach higher concentrations than in open diffusion, with correspondingly shorter ignition delays. It is further anticipated that the ignition delay will become less dependent on external gas environment under these conditions because the chemical runaway is viewed as occurring in the interfacial region where concentration has become insensitive to external pressure.

The advocates of the heterogeneous theory propose that ignition times will vary with pressure in a manner similar to that predicted by the hypergolic theory when the gas pressure is low or the binder

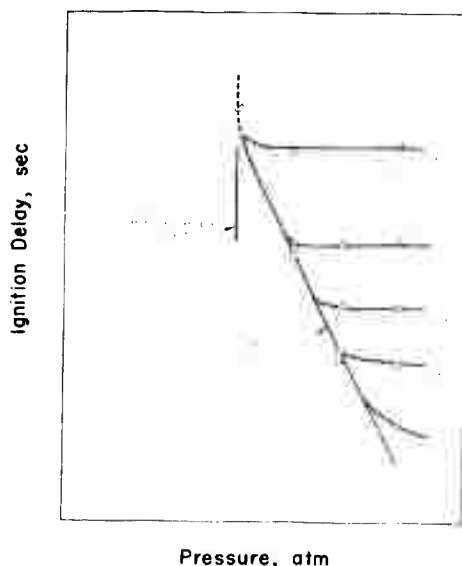


FIG. 3.10. Ignition Delay
as a Function of Pressure
(From Ref. 14).

flexible. Accordingly, the experimental data are plotted as log ignition time versus log pressure, and the observance of a slope similar to that obtained in hypergolic ignition tests is taken as verification of the qualitative model. Such agreement is observed in the domain of low pressure and high heating rates (Fig. 3.10), where conditions most closely approach those assumed in the hypergolic model. On the other hand, it is observed that the ignition delay becomes insensitive to pressure at low heating rates and/or high pressure, consistent with the hypothesis that ignition is being controlled by heterogeneous reactions in confined oxidizer-binder interfaces when pressure rise and concentration are insensitive to external pressure. It is argued that the ignition delay under these conditions is governed primarily by the thermal induction period, which is expected to be correlated by a curve of slope -2.0 in a log ignition delay-log heating rate plot (Fig. 3.11). The available data also tend to support this aspect of the theory, a result which is taken as "proof" of this "confined heterogeneous reaction" aspect of the theory.

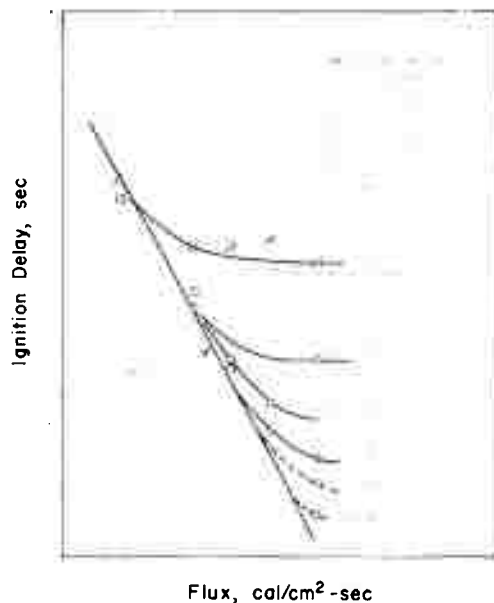


FIG. 3.11. Ignition Delay as a Function of Flux (From Ref. 14).

3.2.2. Discussion of the Heterogeneous Theory.

The emergence of the heterogeneous theory illustrates an unfortunate aspect of the way in which comprehensive understanding of a problem is typically achieved. Prior to introduction of this theory, consideration of heterogeneous mechanisms was conspicuous for its absence, reflecting a limited approach to the ignition problem. This "tunnel vision" aspect of our research was again reflected in the manner of presentation of the heterogeneous theory itself, which was characterized by disdain for other theories and by a web of pseudologic that purported to prove that the heterogeneous theory was "correct" and the other theories were either special cases of the heterogeneous theory,

or unimportant secondary aspects of ignition. Needless to say, this has lead to intensive discussion and public debate by the theoreticians, and to contemplation of "crucial" experiments to prove or disprove theories. This controversy is still continuing, so that no objective resolution is now possible. However, there are a number of issues regarding the heterogeneous theory that need to be spelled out clearly for the sake of order in future debate.

The heterogeneous theory as published to date is a qualitative theory, and hence no quantitative proof of its validity is possible. Attempts have been made to prove the relevance of the theory by comparing the trends of observed ignition delays with trends predicted by hypergolic theory. However, the trends so predicted are based on subjective selection of kinetic parameters in hypergolic ignition tests. The relevance of these parameters has not been established independently, the values are not consistent with observations of steady-state binder pyrolysis (Ref. 35), nor has the relevance of the one-dimensional hypergolic model to three-dimensional heterogeneous ignition with external heating been quantitatively established. The faulty presumption has been made that the initial failure of the gas-phase model to explain experimental observations "disqualifies" a gas-phase mechanism. Claims for relevance of the heterogeneous theory are made in sweeping terms in the presence of only limited experimental data, (e.g., Ref. 4 and 14) of questionable accuracy and relevance (e.g., Ref. 29). These data are usually equally acceptable to interpretation in terms of competitive theories. Under conditions of high pressure and/or low heating rates, where experimental data clearly deviates from the trends characteristic of hypergolic ignition, the "theory" of sub-surface heterogeneous reactions is advanced to explain the low dependence of ignition delay on pressure. Only superficial consideration is given to the three-dimensional aspects of the heat flow that must exist in both the thermal and chemical induction phases of the ignition transient under these conditions. Further, only superficial treatment of the problem of gas flow from interfacial reaction sites is provided in support of the proposed dominant role of interfacial reactions at high pressures. Under conditions of high heating rate and low pressure, experimental results obtained by ignition with an external heat source are observed to exhibit a τ vs. p dependence similar to hypergolic ignition. This result is reported to have been compared with results computed from the hypergolic theory augmented by an external heating term, but this does not appear to have been done in a rigorous fashion. Furthermore, it can be shown by purely qualitative arguments that the mechanisms presumed in the "analysis" could not lead to the τ vs. p dependence ascribed to both analysis and experiment (see Section 5). Independent experiments to establish the effectiveness of heterogeneous reactions at the temperatures involved do not consistently support a dominant rate for such reactions (Ref. 36).

In the face of these deficiencies in existing theory, it appears that the heterogeneous theory should be reviewed and established on a less speculative basis--or advanced with the same candid self-criticism as other theories.

4. GAS-PHASE IGNITION THEORY

Two conspicuous deficiencies of condensed-phase ignition theories are the inability to predict observed dependence of ignition on gaseous environment, and the absence of any recognized condensed-phase exothermic reactions in many propellants. This led to studies of gas-phase ignition, including experimental studies in a shock tube, and analytical studies of gas-phase models designed to conform to the shock tube experiment (Ref. 25, 26, 33). This work, initiated in about 1958, has led to two principal theoretical treatments, the second being similar to, but more sophisticated than, the first. A third analysis, improving on the second has been prepared by the same authors, but is not yet published (Ref. 27).

As reported to date, the gas-phase "analytical" models are one-dimensional, with oxidizer supplied from the environmental gas, with fuel supplied by gasification of the solid (Fig. 4.1). The igniting stimulus is applied by conductive heating from the oxidizing environmental gas, which is assumed to have been abruptly heated by shock compression. In this "step function" conductive heating, the interface temperature rises abruptly to a temperature determined by the temperature difference and thermal diffusivities of the two media. This surface temperature is assumed to remain constant, with a corresponding (temperature dependent) gasification at the surface supplying fuel vapor for the gas-phase reactions. Diffusion of the fuel gas into the oxidizing environmental gas is represented in one-dimension, with exothermic reaction of these gases at a rate dependent on concentration and temperature. Criteria for ignition in the model are based on attainment of some specified temperature or rate of change of temperature. It is recognized that combustion ultimately is sustained by propellant ingredients alone, but assumed that this condition can be assured as a consequence of the reactions of fuel and environmental oxygen represented in the model.

In reviewing the gas-phase model, it is appropriate to note some conspicuous differences from other theories, differences that are related more to the initial and boundary conditions than to the contributing processes. First, in contrast to the hypersonic model, there is external heating as well as chemical heating. Second, in contrast to the condensed-phase models, the heat flow is represented by a constant surface temperature⁷ instead of a constant heat flux and rising surface temperature (thus, there is no thermal induction phase distinct from chemical phase in the ignition interval). Third, the concept of a go, no-go or self-sustaining test of ignition is meaningless, ignition being assured in terms of the initial conditions above - and experimental interruption of ignition being impossible because removal of the igniting stimulus "removes" the reaction zone. These differences pose profound problems insofar as comparison of different theories are concerned.

⁷ In the unpublished work noted above, the constant surface temperature assumption is replaced by a heat balance condition which allows the surface temperature to rise in response to heating by gas-phase reaction.

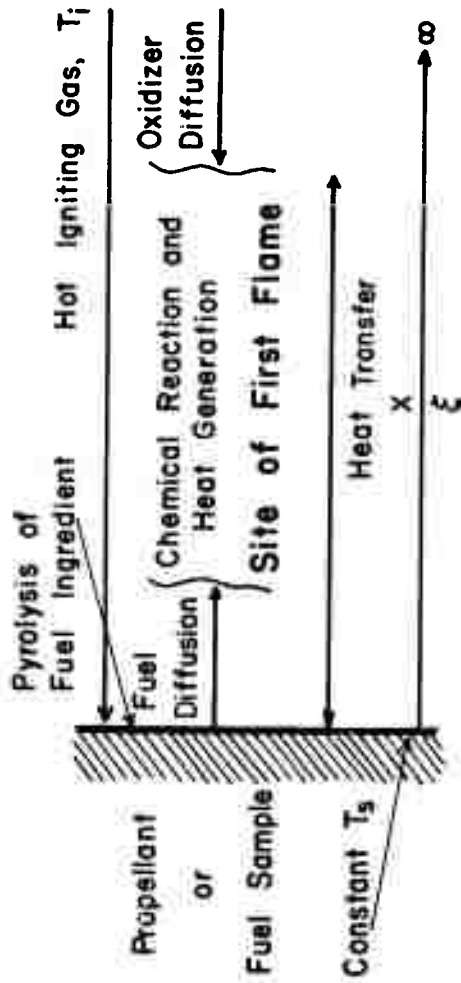


FIG. 4.1. Gas-Phase Ignition of Propellant Samples in Shock Tube.

4.1. EARLY GAS-PHASE THEORY

In conjunction with experimental work on ignition in shock tubes (Ref. 48), McAlevy, Cowan and Summerfield developed a one-dimensional model of ignition of fuel slabs in oxidizing environments, in which it was assumed that an exothermic gas-phase reaction controlled ignition. The analysis will be described in the following paragraphs.

4.1.1. Assumptions of the Gas-Phase Theory.

The McAlevy model was based on the following assumptions:

- (1) The sample starts vaporizing at a constant rate and the mass flux of fuel vapor remains constant up to the moment of ignition.
- (2) The temperature at the sample surface remains constant with time and is given by the 'two semi-infinite body solution', i.e., it is attained instantaneously.
- (3) The fixed oxidizer concentration in the igniting gas remains unaffected by the diffusion of the fuel vapor and the oxidizer diffusion and consumption is unimportant.
- (4) The pressure and density remain uniform.
- (5) Heat transfer to the sample is by conduction only, and the temperature distribution in the gas phase is not affected by the diffusion of fuel vapor.
- (6) Heat is generated in the gas phase by a global second order reaction.
- (7) No heat is generated by solid phase reaction.
- (8) There is little time between runaway reaction in the gas phase and emission of light detectable by the photocell, i.e., ignition time is only the time required for enough fuel to vaporize and give a combustible gaseous mixture.
- (9) Below about 600°K the fuel ingredient vaporizes much more rapidly than ammonium perchlorate, so that only the fuel surface is considered as a source of reactive vapor, the ammonium perchlorate is taken into account only as an inert obstruction, and the same applies to aluminum if present.

4.1.2. Analytical Model.

On the basis that the pyrolyzed fuel vapor, evolved from the sample surface, proceeds through the adjacent gas phase at a rate controlled by mass diffusion, its concentration was represented by

$$C_f = 2\dot{m}_{fs} (t/D)^{\frac{1}{2}} \text{ierfc}(x/2\sqrt{Dt}) \quad (4.1)$$

where in turn \dot{m}_{fs} was assumed to conform with an Arrhenius type equation

$$\dot{m}_{fs} = \nu \rho_f Z_s \exp(-E_s/RT_s) \quad (4.2)$$

ν being the fraction of exposed surface that corresponds to fuel. The gas-phase temperature distribution as a function of time was represented by

$$(\partial T/\partial t) = \alpha(\partial^2 T/\partial x^2) + (Q/\rho c) C_f C_o Z \exp(-E/RT) \quad (4.3)$$

with boundary and initial conditions

For $t \leq 0$: $T = T_i$ at all x

$$t > 0: T = T_s \text{ at } x = 0; T \rightarrow T_i \text{ as } x \rightarrow \infty \quad (4.4)$$

After substituting Eq. 4.1 and 4.2 in 4.3, the authors computed that after a minimum time, $t = t^*$, and at a particular distance, $x = x^*$, the term $\partial T/\partial t$ turns from negative to positive, i.e., it is zero, and as this was taken as the condition for chemical heat generation in the gas phase being equal to the local heat loss, it signifies in the authors' view the beginning of the runaway reaction called ignition. They arrived finally at an equation

$$t^* = KC_o^{-2/3} \text{ or } t^* \propto C_o^{-0.67} \quad (4.5)$$

where K is a constant depending on the nature of the sample and shock tube operating conditions.

4.1.3. Results of Early Gas-Phase Model.

Using published and assumed values for the various parameters involved, the authors made predictions for a composite propellant, 22 percent polyester-styrene/78 percent ammonium perchlorate, which are compared with the observed experimental results in Table 4.1.

TABLE 4.1. Comparison of Predicted and Observed Results

Experiment ^a	Predicted	Observed
Ignition time for propellant in pure oxygen	2 ms	0.2 ms
Ignition time for tests on fuel ingredient	About half that for tests on propellant	Twice that for tests on propellant
Ignition with inert or fuel gas	No ignition	Verified
Dependence of ignition time on oxygen pressure, for pure oxygen, in the range 300-800 psia	$t^* \propto p^{-1.44}$	$t^* \propto p^{-1.77}$
Ignition time for double-base and aluminized composite propellant	Larger than for composite without aluminum	Verified

^aIt was also inferred that catalysts for ignition should be those affecting vaporization and for gas-phase exothermic reactions. This point was verified in the sense that a propellant containing 1 percent Fe_2O_3 exhibited ignition times which were only 2/3 of the corresponding ignition times for the uncatalyzed propellant.

Figure 4.2a shows the graphical correlations obtained by the authors for composite propellants and Fig. 4.2b shows the graphical correlations for double-base propellants. The theory as such does not cover the latter type but it was pointed out (Ref. 34) that the results also support a gas-phase ignition mechanism for double-base propellants, with the oxygen content of the igniting gas also having an active role in the ignition process of those propellants.

4.1.4. Comments on Early Gas-Phase Theory.

The qualitative aspects of this theory constitute a plausible description of the "ignition" of fuel slabs in a shock tube with an oxidative environment. Principal weaknesses from a quantitative viewpoint are:

- (1) Inconsistent assumptions are made regarding conditions at the surface. The assumption of constant interface temperature is based on a heat transfer model which does not allow for reactions, surface

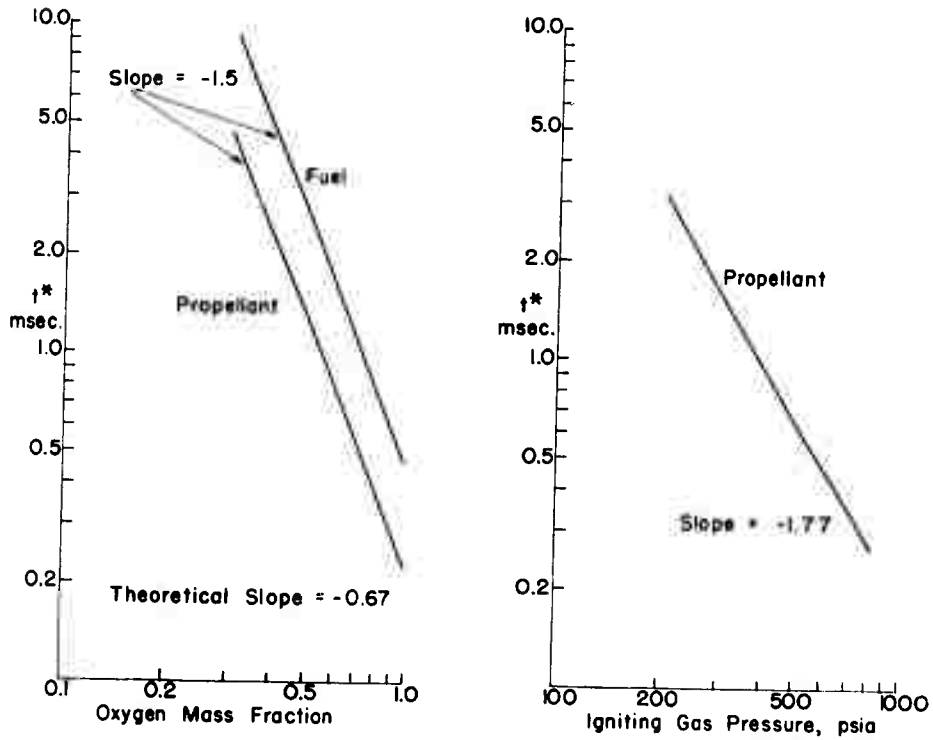


FIG. 4.2a. Composite Propellant: Effect of Oxygen Concentration and Igniting Gas Pressure on Ignition Time.

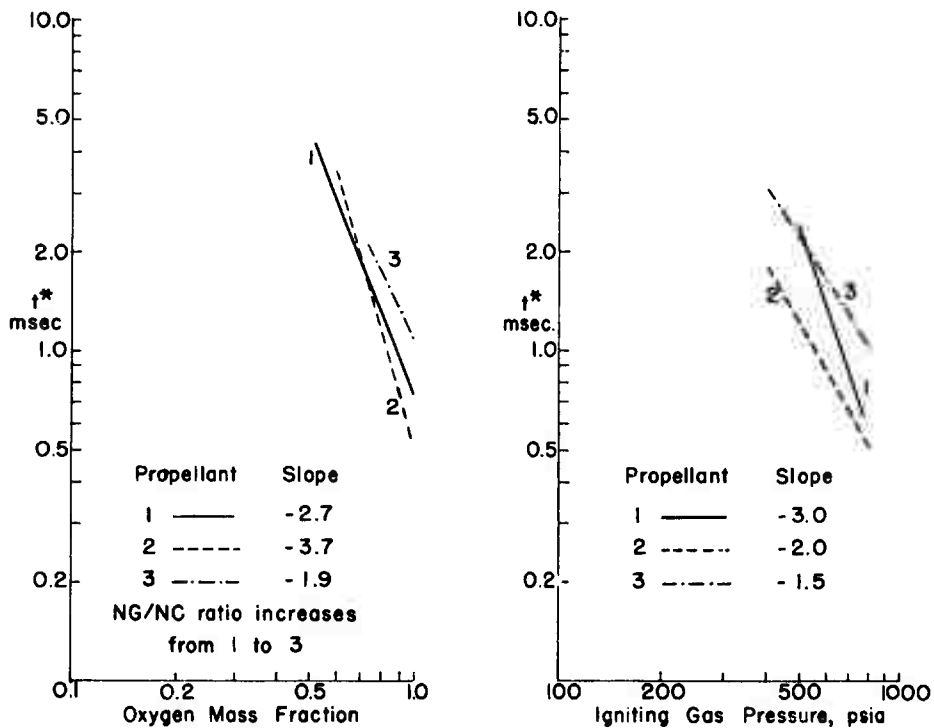


FIG. 4.2b. Double-Base Propellants: Effect of Oxygen Concentration and Igniting Gas Pressure on Ignition Time.

regression, convection, or interface film; thus, the interface temperature is used to calculate a surface gasification whose presence violates the assumptions used in its calculation.

(2) Reaction rates in the gas phase are estimated at each moment on the assumption that prior reaction has not depleted reactants and that there are no residual condensed phase materials accumulating on the pyrolyzing surface.

(3) Ignition in the one-dimensional model is already assured once the initial conditions are applied, in the sense that the diffusion reactions will continue so long as no new change in conditions is introduced.

(4) Ultimately, the question must be asked of the one-dimensional diffusion models, as to the conditions achieved when the oxidizer in the propellant dominates the environmental oxidizer. This question receives only superficial attention. Indeed, it seems quite possible that the solid oxidizer is sometimes already gasifying by the time temperatures are high enough to produce fuel pyrolysis.

(5) The analysis does not provide a satisfactory prediction of ignition trends for propellants, unless rather unreasonable assumptions are made regarding values of kinetic parameters. The calculated mass fraction of fuel at ignition appears to be too small and the discrepancy between predicted and observed ignition times reach as much as one order of magnitude.

As with all solid propellant ignition theories, the lack of independently determined values of kinetic parameters and other physical constants precludes quantitative predictions of ignition behavior by the gas-phase theory. It is noted by McAlevy that the analysis predicts a dependence of ignition time on pressure (constant mole fraction) of the form $t^* \propto p^{-1.44}$ and a dependence of ignition time on mole fraction of oxidizer (constant pressure) of the form $t^* \propto C_O^{-0.67}$. The limited experimental results indicated exponents in both of these relations in the range 1.5 to 1.77, i.e., the ignition time was dependent on absolute oxidizer concentration without much dependence on whether that concentration was varied by pressure or mole fraction. This disagreement between the theory and experimental results has been used as a point in favor of the heterogeneous theory, which is reported to predict ignition rates dependent on absolute oxidizer concentration (Ref. 7). In view of the approximations used in the gas-phase model, disagreement between its predictions and experimental results hardly provides a rational basis for discounting the importance of gas phase processes. Instead, it seems logical to seek a more realistic analytical representation than the "first" model of McAlevy, as was later done by Hermance, Shinnar, and Summerfield (Ref. 26).

4.2. RECENT GAS-PHASE THEORY

In an effort to achieve a more effective representation of gas-phase ignition, Hermance, Shinnar, Wenograd, and Summerfield developed a more realistic analytical model. Most of the published work so far deals with computational procedures intended to solve the relevant differential equations of mass and energy diffusion transfer, but little experimental clarification is offered on how ignition times vary with operating conditions. The very few experimental results apply only to composite propellants and are rather inconclusive.

4.2.1. Assumptions in the Hermance Model.

Rather similar assumptions to those of the McAlevy model were made in order to facilitate the mathematical analysis:

- (1) The solid was assumed to be the source of reactant fuel vapor produced by its sudden contact with the hot igniting gas.
- (2) The sample surface was taken as a fixed plane, one-dimensional and semi-infinite.
- (3) The gas phase chemical reaction rate was assumed to be an instantaneous function of temperature and reactant concentration, second order overall, and given by $C_p C_O^2 \exp(-E/RT)$.
- (4) The density was assumed constant through all the gas phase and independent of temperature.
- (5) The molecular weights of all gaseous species were considered constant and equal.
- (6) The mass diffusivities of all gaseous species were considered constant and equal to the thermal diffusivities of the gas-phase mixture, i.e., $N_L = D/\alpha = 1$.
- (7) Convective transport effects (mass and energy) were neglected.
- (8) The surface temperature of the solid was considered constant at all times and given by the 'two semi-infinite body solution' as in the first treatment.

4.2.2. Analytical Model.

The set of differential equations intended to describe mass and energy transfer in a reacting gas mixture undergoing exothermic reactions were noted as follows:

$$\text{Mass} \quad (\partial C_f / \partial t) = D(\partial^2 C_f / \partial x^2) - C_f C_o Z \exp(-E/RT) \quad (4.6)$$

$$(\partial C_o / \partial t) = D(\partial^2 C_o / \partial x^2) - \sigma C_f C_o Z \exp(-E/RT) \quad (4.7)$$

$$\text{Energy} \quad (\partial T / \partial t) = \alpha(\partial^2 T / \partial x^2) + (Q/\rho c) C_f C_o Z \exp(-E/RT) \quad (4.8)$$

with boundary and initial conditions

$$\text{For } t \leq 0 : T = T_i; C_f = 0; C_o = C_{oi} \text{ at } x > 0$$

$$t > 0 : T = T_s; f(C_f) = \text{const}; D(\partial C_o / \partial x) = 0 \text{ at } x = 0 \quad (4.9)$$

$$T \rightarrow T_i; C_f \rightarrow 0; C_o \rightarrow C_{oi} \text{ as } x \rightarrow \infty$$

where σ in Eq. 4.7 is the stoichiometric ratio in the gas phase chemical reaction as represented by



Two limiting cases for gasification at the fuel surface were considered. In Case 1, the fuel concentration was assumed constant and independent of time, i.e., $f(C_f) = C_f$; and, in Case 2, it was assumed that the fuel mass flux was constant and independent of time or pressure, i.e., $f(C_f) = -D \partial C_f / \partial x = \dot{m}_{fs}$. Case 1 was identified with a condensed phase behaving as a boiling liquid or sublimating solid, and Case 2, with a polymer undergoing irreversible decomposition at constant temperature. The next step in the analysis was to convert the above set of differential equations into the following:

$$\text{Mass} \quad (\partial \eta_f / \partial \tau) = (\partial^2 \eta_f / \partial \xi^2) - \eta_f \eta_o \exp(-1/\theta) \quad (4.11)$$

$$(\partial \eta_o / \partial \tau) = (\partial^2 \eta_o / \partial \xi^2) - \Lambda \eta_f \eta_o \exp(-1/\theta) \quad (4.12)$$

$$\text{Energy} \quad (\partial \theta / \partial \tau) = (\partial^2 \theta / \partial \xi^2) + B \eta_f \eta_o \exp(-1/\theta) \quad (4.13)$$

by using the following dimensionless groups of variables

$$\tau = (\rho Y_{oi} Z) t \quad (4.14)$$

$$\xi = x(D/\rho Y_{oi} Z)^{-1/2} \quad (4.15)$$

$$\theta = RT/E \quad (4.16)$$

$$(\eta_f)_1 = C_f/\rho Y_{fi}; (\eta_f)_2 = C_f(\rho Y_{oi} Z D)^{1/2}/\dot{m}_{fsi} \quad (4.17)$$

$$A_1 = \sigma Y_{fi}/Y_{oi}; A_2 = \sigma \dot{m}_{fsi}/(\rho^3 Y_{oi}^3 Z D)^{1/2} \quad (4.18)$$

$$B_1 = QR Y_{fi}/cE; B_2 = QR \dot{m}_{fsi}/cE(\rho^3 Y_{oi}^3 Z D)^{1/2} \quad (4.19)$$

the resulting boundary conditions being

$$\text{For } \tau \leq 0 : \theta = \theta_i; \eta_f = 0; \eta_o = 1, \text{ at } \xi > 0$$

$$\tau > 0 : \theta = \theta_s; (\eta_f)_1 = 1; (\partial \eta_f / \partial \xi)_2 = 0 \quad \text{at } x = 0 \quad (4.20)$$

$$\theta \rightarrow \theta_i; \eta_f \rightarrow 0; \eta_o \rightarrow 1 \quad \text{as } \xi \rightarrow \infty$$

where the subscripts 1 and 2 above refer to Cases 1 and 2 above (i.e., parameter definitions are chosen differently according to the surface reaction rate assumption). Now a criterion had to be introduced in order to define the ignition event. The authors postulated that ignition would take place at a temperature in the gas phase θ^* somewhat higher than θ_i , and simply defined by $\phi \theta_i$, where the factor ϕ was assigned values between 1.1 and 1.5. So, it was concluded that the dimensionless ignition time τ^* would finally be given by a function of the form

$$\tau^* = f(A, B, \theta_s, \theta_i, \phi) \quad (4.21)$$

and would decrease with decreasing A , (A_1 or A_2), and ϕ values and increasing B , (B_1 or B_2), θ_s and θ_i values.

4.2.3. Results.

The analytical model was studied both by examination of limiting cases susceptible to direct evaluation, and by computer solutions for a range of values of the parameters. The published results concern primarily the trend of ignition time with initial oxidizer concentration, represented first for convenience in terms of a dimensionless time,

$$\tau^* = (\rho Y_{oi} Z) t^* \quad (4.22)$$

Sample data are also plotted for the sake of physical insight in terms of a real time (modified by a reference time t_o^* corresponding to the condition, $Y_{oi} = 1.0$, as a function of initial oxidizer mole fraction. These typical "real-time" plots are shown in Fig. 4.3 and 4.4. The first of these figures corresponds to the case of reversible fuel vaporization (constant fuel concentration at the surface), while the second corresponds to the case of constant vaporization rate (irreversible decomposition at rate determined by the constant surface temperature). The results will be discussed here primarily in terms of the time-mole fraction graphs.

Turning first to the reversible vaporization case, it is shown by limiting arguments that the time-mole fraction relation is reciprocal at high mole fraction (slope -1 in Fig. 4.3 or $\tau^* = \text{constant}$ in Eq. 4.22) and that ignition delay becomes infinite at

$$Y_{oi} < \sigma (\phi - 1) (c \theta_i / Q_f) (E/R) \quad (4.23)$$

The trend at high concentration is essentially determined by the increasing reaction rate as oxidizer concentration is increased, while the increasing sensitivity of ignition delay to concentration at low concentration results from the tendency to deplete the oxidizer in the reaction zone. The limiting concentration for ignition is somewhat artificial, arising from the fact that at this concentration the assumed ignition temperature is just reached when all of the oxidizer is consumed. It is stressed in Ref. 26 that the ignition delay predicted by the model becomes very dependent on the criterion defining ignition when the oxidizer mole fraction is low. This is not surprising since it corresponds to a condition where complete consumption of the oxidizer leaves the reaction products only moderately hotter than the original hot oxidizer (ϕ near 1.0). However, it is difficult to visualize a well-defined ignition event under these conditions, and some experimental methods for detecting ignition would not even indicate ignition under these conditions. In a rocket motor situation it is doubtful

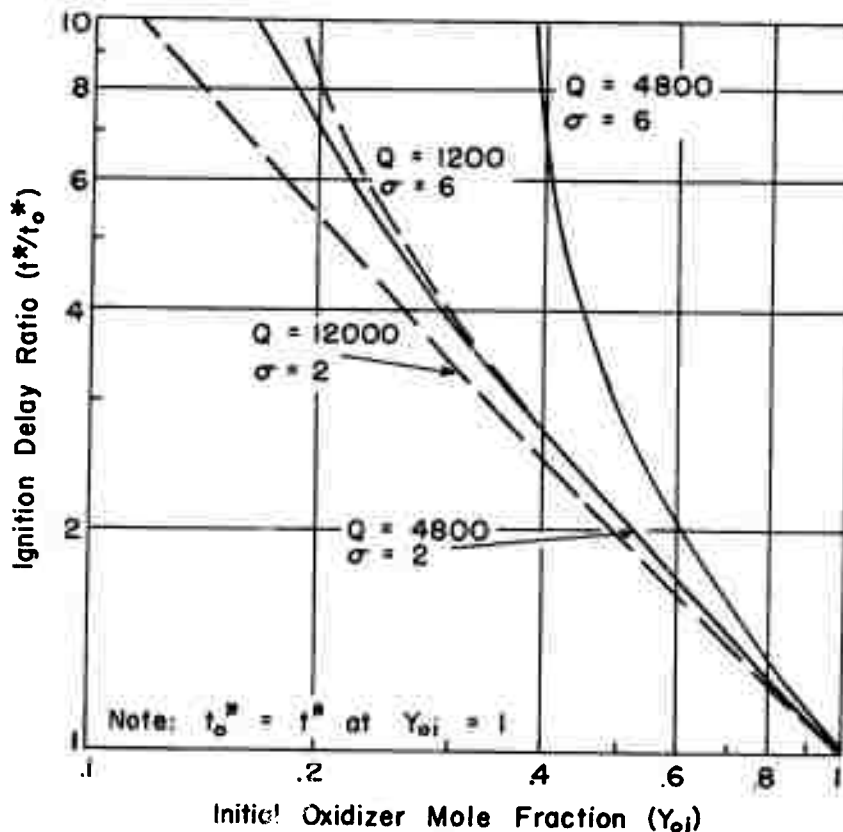


FIG. 4.3. Sensitivity of Real Ignition Delay to Initial Oxidizer Mole Fraction at Constant Pressure. Case 1: Constant C_{fi} case; $B = 3.0$, $\theta_o = 0.3$, $\theta_s = 0.1$, $(E/R) = 4000^\circ K$, $c = 0.3 \text{ cal/gm}^\circ K$, and ignition criterion: $\theta^* = 0.45$ (From Ref. 26, Fig. 11).

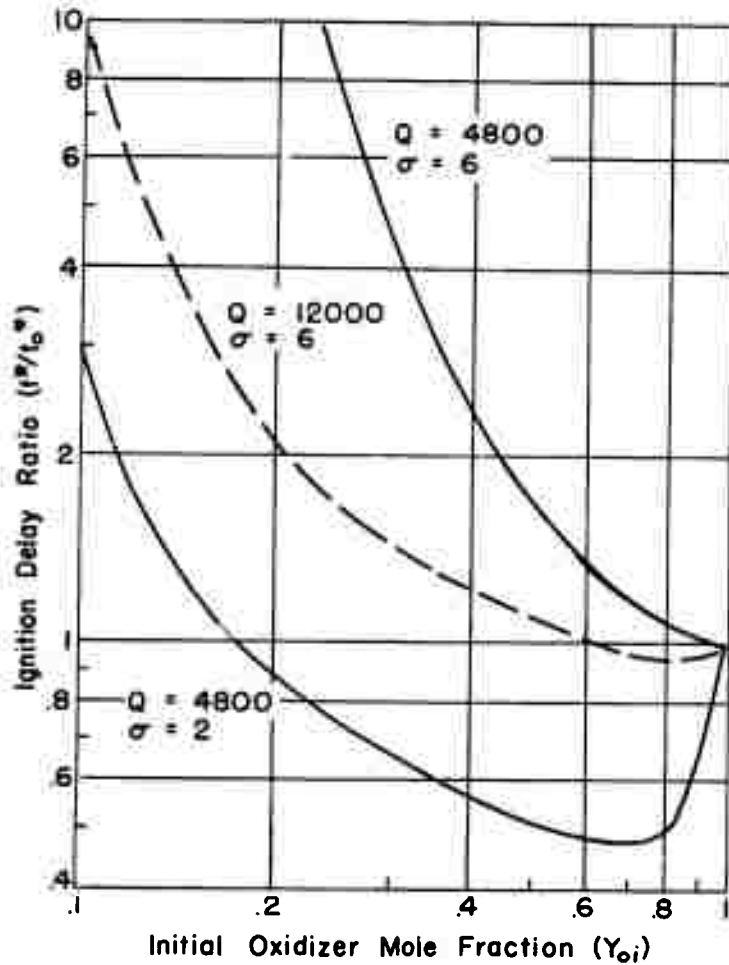


FIG. 4.4. Sensitivity of Real Ignition Delay to Initial Oxidizer Mole Fraction at Constant Pressure. Case 2: Constant \dot{m}_{fsi} at wall, $B^3/\Lambda = 27 \times 10^{-4}$, $\theta_o = 0.3$, $\theta_s = 0.1$, $(E/R) = 4000^\circ\text{K}$, $c = 0.3 \text{ cal/gm}^\circ\text{K}$ and ignition criterion: $\theta^* = 0.39$. (From Ref. 26, Fig. 12)

that so marginal an ignition situation could be tolerated, so the vagueness of definition and measurement may not be in themselves important because they arise under conditions that are not of practical importance.

The concentrations of reactants in the diffusion field are dependent on both mole fraction, Y , and pressure, and each of these variables are susceptible to some independent control in experiments. Thus, it is relevant to examine the effect of pressure as well as mole fraction on ignition time. However, it is not obvious what parameters should be held constant while varying pressure. Of the cases considered by Hermance, the one that seems most relevant to the reversible evaporation model combined the assumptions of constant initial oxidizer mole fraction and constant surface fuel concentration. In this case, the analysis indicated that, for concentrations well above the lower limit for ignition, ignition delay increased slightly with increasing pressure. This trend is noted to be dependent on the assumption of a fixed surface temperature, which is not itself consistent with changing pressure. However, it is not possible to examine this point within the scope of the model.

In the case of the solutions for constant fuel flow (irreversible surface decomposition), the trends of the ignition delay were more complicated. It was shown, for the limiting case of low oxidizer concentration, that ignition delay increased without limit as

$$Y_{oi}^2 \rightarrow \sigma (\phi - 1)(c \theta_i / Q_f)(E/R)(1/\rho^3 ZD) \quad (4.24)$$

As before, this limit is established by the depletion of the oxidizer at low concentration, which limits the attainable temperature rise to a value less than that required to yield the assumed ignition temperature.

From an examination of Fig. 4.4, it is evident that a variety of trends of τ^* vs. Y_{oi} may arise depending on the values of kinetic and other parameters pertaining to the ignition situation. It is shown by a limiting argument that the ignition time is proportional to mole fraction to the minus two-thirds power in the "intermediate" concentration range (at least when it is valid to neglect depletion of reactants, as when Q is large). At high oxidizer concentration, the variation of ignition delay with concentration could be either increasing or decreasing, depending on values of parameters (but in all cases showing a lesser or opposing sensitivity of delay to concentration than in the case of reversible surface vaporization).

The reasons for the varying character of the dependence of ignition delay on concentration at the high-concentration end of the range are not elucidated, but appear to be related to the greater proximity of the reaction zone to the surface, where reaction energy is more easily transferred to the solid. In the case of the constant surface concentration

model, the more rapid depletion of fuel in the presence of high oxidizer concentration is opposed by an increased vaporization rate, which holds the reaction site away from the surface. In the case of the constant fuel flux model, increasing oxidizer concentration moves the reaction site close to the surface where reaction energy is lost to the solid. Although this point is not argued in the references, it seems likely that the occurrence of a reversal in the ignition delay concentration relations at high concentration may be due to this tendency for the reaction site to move towards the isothermal surface. In a real physical situation, the surface temperature would presumably increase, so that the trends predicted at high concentration are probably unrealistic. This shortcoming is apparently remedied in a forthcoming analysis (Ref. 27).

In considering the effect of pressure on ignition for the irreversible fuel vaporization model (Ref. 25), some assumptions must again be made regarding the effect of pressure on fuel vaporization rate. Lacking any unique basis for choice in the model, Hermance reported the trend of delay with pressure for various values of δ in the assumed relation $\dot{m}_{fsi} \propto p^\delta$. For high values of δ , the ignition delay was predicted to decrease with increasing pressure, the actual sensitivity depending on other parameters. Because of the complex range of results obtained for the irreversible vaporization model, no simple generalization of trends with pressure is possible. As in the case of the reversible vaporization model, the model is not well suited to prediction of trend with pressure because a concurrent trend of surface temperature is likely in an experiment but not established in the model. Again, this shortcoming is apparently remedied in Ref. 27.

Considerable stress is put on the sensitivity of the computed ignition time to the exact definition of ignition, and the computed results do indeed show the time to be a sensitive function of ϕ at low oxidizer concentration, or when the activation "threshold" temperature E/R is not much higher than the environmental gas temperature, T_0 . In the case of low oxidizer concentration, this sensitivity is due to the tendency for depletion of the oxidizer in the reaction zone to slow the temperature rise rate compared to that dictated by temperature dependence of kinetic rates. In the case of low activation energy, the sensitivity to definition of ignition is due to the relatively low energy required to achieve ignition. Under less tenuous ignition conditions, the ignition time is seen to be relatively insensitive to criterion for ignition, although more sensitive than in other ignition theories, which do not depend so heavily on diffusion processes.

The plausibility of determining overall activation energies and effective order of reaction from the ignition delay trends is explored in terms of the predictions of the model, and it is made clear that the dependence of ignition on diffusion processes invalidates any simple interpretation of ignition trends in terms of kinetic parameters. The paper gives the impression that this result was surprising to the authors. In the absence of preconceptions, it seems obvious that such

a result would apply, unless the masking contribution of diffusion processes could be removed from the experiment or accounted for quantitatively in the interpretation.

4.2.4. Discussion.

4.2.4.1. Comparison of the McAlevy and Hermance Models.

The physical concepts involved in the Hermance model of gas-phase ignition are the same as those of the McAlevy model, although a somewhat more sophisticated and flexible representation is used. Both models picture the solid as a semi-infinite fuel slab suddenly exposed to a hot oxidizing, gaseous environment, with a constant interface temperature assumed so as to decouple the analysis of the gas phase processes from the heat transfer in the solid. Consistent with this simplification, both models use simplified models of fuel vaporization at the surface that pertain to a constant-surface-temperature model. The Hermance model considers two limiting cases of fuel vaporization, one corresponding to irreversible decomposition and the other to reversible vaporization (the McAlevy model considers only the former). Both analyses neglect regression of the surface, accumulation of non-reacting material at the surface, convection of fuel gas away from the surface (as opposed to molecular diffusion), variation in physical properties of materials in the diffusion zone (e.g., density, heat capacity, heat conductivity, etc.). The McAlevy model represents the diffusion in the gas phase as proceeding without effect of temperature change or depletion of reactants, while the Hermance model considers depletion, but assumes the diffusion of mass and heat to be related by the condition that the Lewis number equals one. The comparability of the ignition criteria in the McAlevy and Hermance models was examined by Hermance, who noted that the temperature-time reversal criterion of McAlevy could be satisfied much sooner in the ignition interval than the criterion of achieving a specified temperature above the initial gas temperature as in the Hermance model. This was in line with the general observation in the Hermance paper that ignition delay time was relatively sensitive to choice of definition of ignition (relatively sensitive compared to ignition controlled by kinetics of a one-step exothermic reaction).

4.2.4.2. Relation of Gas-Phase Theory to Other Theories.

In comparing the gas-phase theories to other quantitative theories, there are two conspicuous attributes of the model that should be emphasized. First, the model does not exhibit the externally controlled thermal induction interval encountered when the surface is subjected to finite heat fluxes. The surface temperature is instead raised instantaneously to a decomposition temperature, and chemical reactions start immediately as they do in the hypergolic ignition model. This tends to dramatize the dependence of ignition delay on ignition criterion, (and especially so when activation energy is low or initial gas temperature is high). Thus, the emphasis on this point in the Hermance paper would be less relevant to, say, arc-image ignition situations, where the initial temperature is low, and reactions start only after an appreciable heating

period. The importance of diffusion will, however, still make the ignition criterion a relatively critical matter in any gas-phase model, simply because the otherwise dominant role of the exponentially temperature-dependent reaction rate is modified by diffusion controlled reactant concentration.

The second singular attribute of the present gas-phase model, as compared to other current theories, is the fact that the oxidizer gas is hot. This is not so in the hypergolic model and not so in radiant heating models. The importance of this to gas-phase models in general is that the diffusion reaction sites will normally be more removed from the surface in a hot gas model than in cold gas models, because the required temperatures are available there. It is not feasible to assess the importance of this difference at present, but it is difficult to see how experimental data acquired by radiant-heating experiments could be rationalized by the present model. Likewise, a comparison of predictions of constant heating models with those of present gas-phase models would be inappropriate without detailed justification.

It is particularly important to note that, even in the relatively simplified representation of gas-phase ignition provided by the present models, the variation of ignition delay with such experimental variables as oxidizer concentration and pressure is extremely complex, more so than is predicted by hypergolic and solid-phase theories. At the present time it would be very difficult to test the relevance of the models experimentally by examining trends of ignition delays, and quite impossible to go further by this means and conclusively test the relevance of the actual gas-phase mechanism itself.

4.2.4.3. Further Information From the Gas-Phase Theory.

The reporting of the gas-phase analysis in Ref. 25 and 26 was carried out in a scholarly and objective manner. The grouping of variables was exploited to great advantage, the exploration of limiting cases was pursued effectively, and the assumptions of the model and their effect on relevance of the model were discussed candidly. For more satisfactory physical insight, a more detailed examination of the model and the computer results would be desirable. As an example, the question of adequacy of the constant-surface-temperature assumption could be explored better if information from the computer runs were available describing the dependence of location of the ignition site on oxidizer mole fraction. More details are apparently included in the unpublished report, Ref. 27. As another example, data regarding the concentrations and amount of reactants consumed (perhaps only at the time and place of "ignition") would be instructive to help judge the plausibility of parameter values and help assess the conditions under which depletion of reactants is a major factor in determining ignition time. It is not clear how such data should be made available, but it would enhance the value of the original work. This problem is, of course, not unique to this particular research project.

5. DISCUSSION

5.1. PURPOSES OF A REVIEW

The present report was undertaken because it was felt that the desultory character of past work on ignition theory could be avoided in future work if an adequate starting point could be provided for future research (the term desultory refers here to the lack of continuity or comparability of work in the last 20 years, not to the individual contributions of the various research teams). The review would collect together most of the relevant work, restate it in a common body of notation, and present it in an organized fashion that would bring out the broader relationships among the existing theories (which otherwise tend to be lost in the welter of publications, notations, assumptions, computational details and changing investigators in research laboratories). These goals are in part served by the preceding portions of this report, but there remains a need for better perspective. In the following, we shall try to describe the ignition process in terms that will encompass all of the mechanisms considered in the various theories, note where these theories fit in this description, and examine the relation of the analytical models to physical reality. This last goal will inevitably lead to criticism of current theories, with regard to relevance to real behavior, and in some cases with regard to correctness of the arguments advanced.

5.2. THE IGNITION "SEQUENCE"

Current analytical models of propellant ignition represent the process in terms of one-dimensional models consisting in each case of a semi-infinite slab of fuel or homogeneous monopropellant, stimulated at the surface in the presence of an oxidizing atmosphere. Although there are profound limitations to such models, we will defer discussion of the limitations in order to concentrate first on the existing models.

It is convenient to start with the situation where the propellant surface is subjected to external heating without chemical activation. After the onset of heating, the temperature in the vicinity of the surface rises in a manner dependent on the particular heating process, and after a time, chemical reactions start and more or less precipitously replace the external heat source as the controlling stimulus. Before examining this sequence further, it should be stressed that current quantitative models do not all conform to this picture, the hypergolic theory lacking the external heat source and the gas-phase theory assuming a step-rise in surface temperature with concurrent onset of surface reaction. Because these differences in the models complicate their comparison (while being nonessential to the mechanistic arguments), we will direct our attention first to behavior to be expected when constant external heating is applied.

Under the influence of constant external heating, the applied heat, heating rate, and surface temperature rise will be related through Eq. 2.15 until onset of chemical reactions. After a period of time that depends upon the kinetics of the propellant ingredients and the value of the external heating rate, reactions will start at or near the propellant surface. These may consist of exothermic decomposition of the solid to a condensed or gas product (condensed-phase theory), endothermic decomposition of the solid to a fuel gas (gas-phase theory), or heterogeneous reaction of the environmental gas with the solid (heterogeneous theory).⁸ The decomposition or reaction is usually presumed to follow an Arrhenius rate law dependence on temperature, with a dependence on gas composition included in the heterogeneous theory and the reversible vaporization case of the gas-phase model.

Considering the surface temperature-time history during external heating and initial chemical reaction, the behavior is illustrated qualitatively in Fig. 5.1. Section 1 of the curve corresponds to behavior before onset of chemical reaction, under the influence of a constant external heating rate (see Section 2.1.1.2 of this report). The extension of the curve labelled "2" is descriptive of the behavior when exothermic heating occurs first in the condensed phase (see Section 2.2 of this report). The temperature rises precipitously after onset of reaction, the exact rate being sensitive to the activation energy of the reaction. For more complicated reaction processes, the time and steepness of the temperature rise may be related to the accumulation of active intermediate reaction products, but this class of behavior has received little consideration in theories of condensed-phase ignition of solid propellants, probably because of greater analytical complexity and lack of sufficient knowledge of relevant reaction processes to warrant such analytical complexity.

In the case where the first exothermic reaction is a heterogeneous one between an oxidizing environmental gas and the propellant binder, the occurrence of the precipitous temperature rise will be dependent on the concentration and nature of the oxidizing gas. However, the dependence on environmental gas as depicted in the hypergolic theory will be minimized in the present case, because the "induction" time which comprises most of the ignition time in the hypergolic theory is compressed in the present case by the continued temperature rise due to the external heating. Thus, the precipitous temperature rise indicative of ignition (extension labelled "3" of Fig. 5.1) will look much like the curve for condensed-phase ignition, although it should be mildly dependent on oxidizer concentration and pressure in the environmental gas.⁹

⁸ As noted in Fig. 1.1, a number of other sequences of reactions are possible.

⁹ This relative insensitivity to environmental gas is contrary to arguments in Ref. 14, but consistent with the view of Ref. 53.

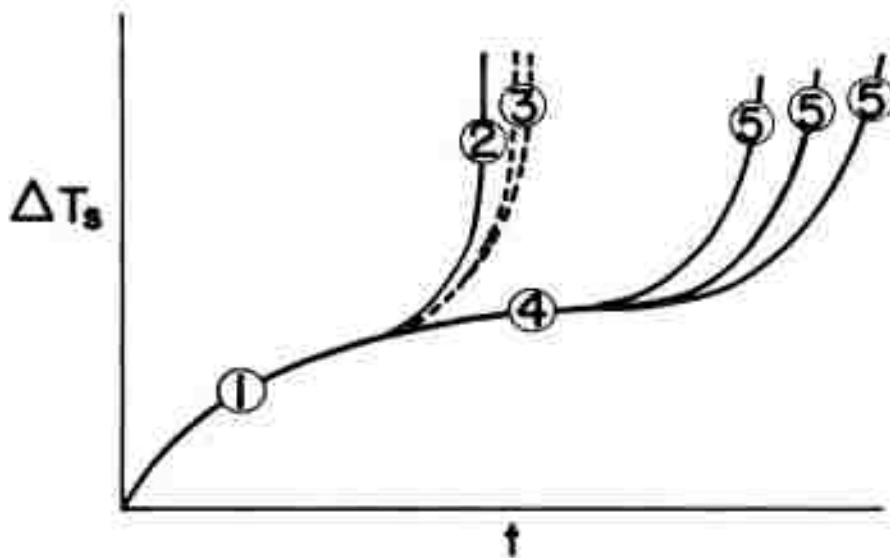


FIG. 5.1. Qualitative Trends of Surface Temperature Rise During Constant-Flux Heating and Ignition, Showing Comparison of Condensed Phase, Heterogeneous and Gas-Phase Controlled Cases. 1. Heating at constant q ; 2. Precipitous temperature rise due to condensed-phase reaction; 3. Precipitous temperature rise due to heterogeneous reaction; 4. Delay in temperature rise due to endothermic decomposition; 5. Precipitous temperature rise due to diffusion reaction.

The extension labelled "4" in Fig. 5.1 corresponds to a situation where the first reaction is an endothermic decomposition of the surface, followed by exothermic reaction in the gas phase. The exothermic reaction rate in the present case will be sensitive to oxidizer concentration and pressure if diffusion of the fuel gas into the oxidizer gas is necessary, even though external heating is continued. This would be the case if the endothermic reaction were fuel pyrolysis and the exothermic reaction oxidation of the fuel gas as in Section 4. However, it should be emphasized in this context that the existing gas-phase models do not conform to the situation in Fig. 5.1 because a constant external heating rate is not assumed in those models. Those models do, however, illustrate the strong dependence of ignition behavior on environmental gas composition and pressure, which would be expected also in the constant-external-heating situation.

Only limited attention has been given to the case of gas-phase ignition in which the reactants all originate from decomposition of a single ingredient. This type of ignition is not dependent on diffusion, and hence would not be expected to conform to the environmental-gas-dependent predictions of current gas-phase models. However, this type of ignition is very like that exhibited by ammonium perchlorate, and by nitrocellulose at low pressure, and hence is of more than passing interest.

5.3. COMPARABILITY OF THEORIES

It is singularly unfortunate that the three principal quantitative models of ignition were all developed with different representations of the external heating, since it prevents valid comparison of the predictions of the theories. Likewise, a valid comparison of experimental results with all three classes of theories is at present impossible, since the experiment cannot be constructed to conform to all three classes of models at once. These difficulties have often been ignored in arguments regarding agreement between experiments and theories, with the result that the arguments themselves only confused the issues further. It is not clear that there was any advantage to the particular choices of heating conditions chosen in the present models, except conformance with some particular experiments whose particular merits are yet to be fully compared. It seems likely that future analytical and computer work will be oriented around condensed-phase, heterogeneous and gas-phase models with the same representation of external heating - perhaps with constant external heating, as approximated in arc-image furnace ignition experiments.

Another problem in comparison of theories is the difference in choice of ignition criteria. In the case of the gas-phase models this was shown to be a serious source of "error" in predicting ignition delay. A high degree of arbitrariness exists in the definition of ignition in the models, which cannot be eliminated by reference to the real ignition process because the models are not sufficiently realistic representations of practical ignition of real propellants. Under those conditions where a truly decisive runaway event is not predicted by the model, it seems inappropriate to report computer results simply in terms of an arbitrarily chosen ignition criterion, nor to compare predictions of theories simply in terms of such arbitrary criteria.

5.4. RELEVANCE OF THEORIES TO PROPELLANT IGNITION

The difficulties of accurately representing so complex and versatile an event as ignition of solid propellants are truly awesome. The decomposition kinetics of even the simplest propellant ingredients are usually unknown, or known only at low temperatures. The physical and thermal properties are usually known only at room temperatures, if at all.

The reactions between propellant ingredients or primary products are extremely complex. Because the problem is transient, recourse must be made to rate constants for the relevant reactions and these constants are rarely known. In fact, there is reasonable grounds for debate as to whether the solid oxidizer or the binder will decompose first. The propellant is usually chemically, physically and optically heterogeneous on a dimensional scale that cannot be ignored in accurate representation of the surface layer heating. In the gas phase, it is more typical that the oxidizing species originate from decomposition of the solid oxidizer than from the environmental gas, with the oxidizer gas diffusing to the site of the fuel (or vice versa) by a three-dimensional diffusion in the environmental gas.

In contrast to this, the quantitative theories all assume that the propellant is homogeneous in all respects,¹⁰ and that the oxidizing gas originates in the environmental gas. In the hypergolic and gas-phase theory, the solid is effectively a fuel slab, actually incapable of self-sustained burning. The chemistry in all models is represented by global one-step reactions, simplified in the condensed-phase and hypergolic theories to one such reaction. The unknown physical and kinetic constants relevant to the systems appear in the theories as undetermined parameters, frequently "evaluated" by a best fitting procedure of computed ignition delays to experimentally observed delays. The naivety of such fitting procedures in the face of the highly approximate nature of the models is pointed out by the comments of Hermance regarding determination of activation energies and reaction orders from slopes of ignition delay curves.

In the face of these criticisms, one might wonder whether theory has any value for the subject of propellant ignition. This classical question is just as hard to answer decisively in the field of ignition as in other fields. It seems clear from the earlier comments that little or no understanding would be possible without theory, that the intelligent design of experiments is dependent on an ability to ask reasonably precise questions stemming from theory. It is not necessary that the analytical models be rigorously correct in all details in order to be of value, but it is necessary that they provide a basis for posing meaningful questions that are susceptible to experimental test.

It seems clear that the non-comparability of the existing models seriously compromises the formulation of "reasonably precise questions". Even so, the level of understanding of ignition processes has been greatly enhanced by the present theories, as has the design of current experiments. As a result, much more is known about how propellants ignite, and about what should be done in the future to further elucidate ignition processes. It seems likely that a combination of theory and matching laboratory

¹⁰ Allowance for a non-participating ingredient is sometimes made, but without any consideration of propellant microstructure.

experiments will, in the future permit identification of the controlling steps in ignition of real propellants; how these steps change as a function of propellant, environment, and ignition stimulus; and how these changes should be allowed for in ignition system design. Until analytical models with consistent representations of initiating stimuli are developed and until experiments consistent with these models are also available, little more scientific progress seems likely.

Appendix

A3. DIMENSIONAL ANALYSIS AND SOLUTIONS FOR
SPECIAL CASES OF THE HYPERGOLIC THEORY

A dimensional analysis of the hypergolic model is presented, and, in addition, three special cases of the theory are solved analytically. The dimensional analysis is of primary value in reducing the number of quantities needed to describe the system and in determining which ones of the original parameters have a similar effect on the solution. The special cases can be used as a test of the validity of conclusions made concerning the general model, since they are included in the general model, and statements regarding the general model must therefore be compatible with the results obtained for the special cases.

A3.1. DIMENSIONAL ANALYSIS

Since insight into the behavior of the hypergolic ignition model may be obtained by use of dimensional analysis (Ref. 25, p. A-21), a dimensional analysis was made of Eq. 3.1 through 3.16. Controversy has arisen concerning the last two terms of Eq. 3.15. For the range of parameters of interest they appear to be of secondary importance and hence are not included in the analysis.

The analysis yields four functional relationships involving the independent variables, t and x ; the dependent variables, T_g , T_c , C_{pg} , C_{og} ; and the system parameters. Since the ignition time is of primary importance, a group containing time is considered as a dependent variable, while the dimensionless temperature of the solid is considered as an independent variable. Formally, the result of the analysis may be written as

$$g_j = f_j \left(x^2/a_c t, T_c/T_i; a_g/a_c, a_c/D_o, k_g/k_c, \right. \\ \left. E/RT_i, D_o Q_s C_{oi} / T_i k_c \right) \quad (A3.1)$$

where

$$g_1 = C_{og}/C_{oi}, g_2 = T_g/T_i, g_3 = Q_s C_{oi}^a \sqrt{a_c} t / T_i k_c,$$

and

$$g_4 = D_p C_{pg} / \psi D_o C_{oi}$$

When surface temperature is considered, $x^2/a_c t$ becomes zero, leaving g_3 as the only group involving Z and t . Hence, it may be concluded that, for dimensional similitude at the surface, t is inversely proportional to Z^2 .

The expression for the dimensionless time required to heat to a specified dimensionless surface temperature is

$$Q_s C_{oi}^a Z \sqrt{a_c t} / T_i k_c = f_3 (T_s/T_i; a_g/a_c, a_c/D_o, k_g/k_c, E/RT_i, D_o Q_s C_{oi} / T_i k_c) \quad (A3.2)$$

and if diffusion is not limiting, then $Q_s C_{oi}^a Z \sqrt{a_c t} / T_i k_c$ is a function only of a_g/a_c , k_g/k_c , and E/RT_i . For fixed values of these three latter parameters, the ignition time is proportional to $T_i^2 k_c^2 / Q_s^2 C_{oi}^2 a_c$.

If on the other hand the left side of Eq. A3.2 is set equal to infinity, the equation may be considered as a diffusion limited case, since it would correspond to setting Z or t equal to infinity. The unknown function then becomes an expression for determining the limiting initial oxidizer concentration for which ignition could occur. The dimensionless concentration, modified by multiplying by the square root of a_c/D_o (in order to represent it in a form which occurs in a later model), becomes $Q_s C_{oi} \sqrt{D_o a_c} / T_i k_c$ which for a given value of T_s/T_i is a function of only a_g/a_c , a_c/D_o , k_g/k_c , and E/RT_i . The term involving oxidizer concentration would be a limiting vertical asymptote on a t^* vs. C_{oi} curve for a fixed set of values of the parameters.

If the loss of heat to the gas phase by conduction is considered to be unimportant, then a_g/a_c and k_g/k_c may be neglected, and Eq. A3.2 reduces to

$$Q_s C_{oi}^a Z \sqrt{a_c t} / T_i k_c = f_3 (T_s/T_i; a_c/D_o, E/RT_i, D_o Q_s C_{oi} / T_i k_c) \quad (A3.3)$$

If diffusion is not limiting and the concept of a fixed ignition temperature is assumed, then for a fixed initial temperature

$$Q_s C_{oi}^a Z \sqrt{a_c t} / T_i k_c = f_3 (E/RT_i) \quad (A3.4)$$

A3.2. ANALYTICAL SOLUTIONS OF SPECIAL CASES

The behavior of the hypergolic ignition model was further investigated by considering three special models which were analytically tractable.

The first model assumed that the surface reaction was controlled by diffusion, the second model assumed a kinetically controlled reaction with zero activation energy, and the third model assumed a first order reaction with zero activation energy. These special models describe the behavior of the "hypergolic model" under limiting sets of conditions, and thus provide a test of the validity of generalized predictions made concerning the "hypergolic model." The solutions for the three special models may be expressed in terms of the dimensionless variables and parameters obtained in Section A3.1.

A3.2.1. Diffusion Controlled Ignition.

The diffusion controlled model is described by the following set of equations.

$$(\partial T_c / \partial t) = \alpha_c (\partial^2 T_c / \partial x^2) \quad (A3.5)$$

$$(\partial C_o / \partial t) = D_o (\partial^2 C_o / \partial x^2) \quad (A3.6)$$

$$(\partial T_g / \partial t) = \alpha_g (\partial^2 T_g / \partial x^2) \quad (A3.7)$$

$$T_g(x, 0) = T_c(x, 0) = T_i \quad (A3.8)$$

$$C_o(x, 0) = C_{oi} \quad (A3.9)$$

$$C_o(-\infty, t) = C_{oi} \quad (A3.10)$$

$$T_g(-\infty, t) = T_i \quad (A3.11)$$

$$T_c(\infty, t) = T_i \quad (A3.12)$$

$$T_{gs} = T_{cs} \quad (A3.13)$$

$$C_{os} = 0 \quad t > 0 \quad (A3.14)$$

$$-Q_s D_o (\partial C_o / \partial x) = -k_c (\partial T_c / \partial x) + k_g (\partial T_g / \partial x) \quad \text{at } x = 0 \quad (A3.15)$$

Since the concentration field is uncoupled from the temperature fields, it may be calculated from the temperature analog (Ref. 20, p. 59) and the result used in the calculation of the temperature fields. The equation for the solid-phase temperature is

$$(T_c / T_i) - 1 = \frac{Q_s \sqrt{D_o \alpha_c} C_{oi} \operatorname{erfc}(x / 2 \sqrt{\alpha_c t})}{k_c T_i [1 + (k_g / k_c) \sqrt{\alpha_c / \alpha_g}]} \quad (A3.16)$$

and for $x = 0$ the time dependency disappears. Therefore the surface reaches an instantaneous maximum value. Since the surface reaches an instantaneous maximum value, a plot of ignition time vs. concentration is meaningless if a surface ignition temperature is assumed. In this case the occurrence of ignition would depend on whether or not the initial concentration of gaseous oxidizer was at a threshold value. The threshold value of oxidizer concentration in turn would depend on the pressure, since the diffusion coefficient is approximately proportional to the reciprocal of the pressure. When an initial oxidizer concentration is varied by changing the oxidizer mole fraction, the surface temperature rise is directly proportional to concentration, while the surface temperature rise is proportional to the square root of the oxidizer concentration when the concentration is changed by varying the pressure. This model assumes infinite reaction kinetics and is therefore only a limiting condition which would never occur in practice.

A3.2.2. Kinetic Controlled Ignition, Zero Activation Energy.

The second model assumed the kinetics were controlling and that the reaction was of order a , with a zero activation energy. The mathematical description of the temperature fields is given by Eq. A3.5, A3.7, A3.8, A3.11, A3.12, A3.13, and the following two equations:

$$C_o(x,t) = C_{oi} \quad (A3.17)$$

$$Q_s Z C_{oi}^a = -k_c (\partial T_c / \partial x) + k_g (\partial T_g / \partial x) \quad \text{at } x = 0 \quad (A3.18)$$

The equation for the condensed phase temperature is

$$T_c / T_i - 1 = \frac{2 Q_s Z C_{oi}^a \sqrt{a_c t} \operatorname{ierfc}(x / 2 \sqrt{a_c t})}{T_i k_c [1 + (k_g / k_c) \sqrt{a_c / a_g}]} \quad (A3.19)$$

If a fixed non-dimensional ignition temperature at the surface is assumed, this model would predict that a log - log plot of t^* vs. C_{oi} would have a slope of $-2a$. The result is independent of whether the concentration of oxidizer is changed by changing the mole fraction of oxidizer while holding the pressure constant, or by changing the total pressure while holding the mole fraction constant. This model would be expected to be independent of pressure, since diffusion is not involved. A complete determination of the effect of pressure would of course require examining the effect of pressure on all the parameters, not just the diffusion coefficient. The rate of increase of temperature at the surface would not be an adequate criterion for this model, since the rate is infinite at t equal to zero and decreases with time.

A3.2.3. Zero Activation Energy, First Order Reaction.

The third model assumes zero activation energy and a first order reaction. In some respects this model may be considered to overlap the previous two models. The mathematical description of the model is given by Eq. A3.5 through A3.13, Eq. A3.15, and the following equation:

$$-D_0(\partial C_0/\partial x) = C_0 Z \quad \text{at } x = 0 \quad (A3.20)$$

In this system of equations the diffusion equation is uncoupled and may be solved to determine the concentration field of the oxidizer. The temperature analog of the diffusion equation is given in Ref. 20, p. 70. The solution in terms of the concentration model is

$$C_{0s} = C_{0i} \exp Z^2 t/D_0 \operatorname{erfc} Z\sqrt{t/D_0} \quad (A3.21)$$

and the Eq. A3.15 may be replaced by

$$Q_s Z C_{0i} \exp Z^2 t/D_0 \operatorname{erfc} Z\sqrt{t/D_0} = -k_c \partial T_c/\partial x + k_g \partial T_g/\partial x \quad \text{at } x = 0 \quad (A3.22)$$

The solutions for the temperature fields were then obtained by the method of the Laplace transformation, and the resulting equation for the temperature of the solid phase was

$$(T_c/T_i)-1 = \left\{ \frac{Q_s \sqrt{D_0 a_c} C_{0i}}{T_{ikc} [1 + (k_g/k_c) \sqrt{a_c/a_g}] } \right\} \left\{ \operatorname{erfc}(x/2\sqrt{a_c t}) - \exp[(Zx/\sqrt{D_0 a_c}) + Z^2 t/D_0] \cdot \operatorname{erfc}[(x/2\sqrt{a_c t}) + Z\sqrt{t/D_0}] \right\} \quad (A3.23)$$

The equation when evaluated at the surface reduces to

$$(T_s/T_i)-1 = \left\{ \frac{Q_s \sqrt{D_0 a_c} C_{0i}}{T_{ikc} [1 + (k_g/k_c) \sqrt{a_c/a_g}] } \right\} \left\{ 1 - \exp(Z^2 t/D_0) \cdot \operatorname{erfc}(Z\sqrt{t/D_0}) \right\} \quad (A3.24)$$

Some idea of the effect of heat loss to the gas phase by conduction can be made by computing the value of the expression

$$1 + (k_g/k_c) \sqrt{a_c/a_g}$$

which occurs in the denominator of Eq. A3.24. A value of 1.007 was computed for the expression using the numerical values of the parameters contained in the following:

Item	Gas phase	Solid phase
Specific heat (cal/gram°C)	0.30	0.4
Density (grams/cm ³)	2.85 x 10 ⁻³	1.75
Thermal conductivity (cal/sec cm°C)	4 x 10 ⁻⁵	0.001

Since the expression would be equal to one if heat loss to the gas phase by conduction were neglected, the calculation would indicate only a very small effect due to conduction of heat into the gas phase. The heat loss to the gas phase may become important at high pressures. It must be borne in mind that the calculation has been shown to be applicable to the special models and can only be used qualitatively when considering the more complex model in which E is other than zero and a is not restricted to one. The foregoing discussion does not preclude the possibility that the complete model may have the same type of dependency on thermal properties.

The temperature-time derivative at the surface, as in the previous two models, cannot be used as a criterion of ignition, since the value of the derivative starts at infinity and decreases with time.

Equation A3.24 describes a system which is kinetically controlled when Z is very small or D is very large. The expression in braces on the right of Eq. A3.24 may be written as $1 - \exp(Z^2 t/D_0) + \exp(Z^2 t/D_0) \operatorname{erf} Z\sqrt{t/D_0}$ and, when this expression is expanded in terms of $Z\sqrt{t/D_0}$ with $Z\sqrt{t/D_0}$ assumed much less than one, the expression may be approximated by $(2/\sqrt{\pi})Z\sqrt{t/D_0}$. Therefore the limiting slope on a log - log plot of ignition time vs. concentration would be -2. The limiting form of the equation is identical to Eq. A3.19 when a is set equal to one and the latter equation is evaluated at the surface.

Diffusion processes are controlling when $Z^2 t/D_0$ is large. In the limit $\exp(Z^2 t/D_0) \operatorname{erfc} Z\sqrt{t/D_0}$ approaches zero and Eq. A3.24 reduces to the time independent Eq. A3.15 evaluated at the surface.

Equation A3.24 is plotted as a solid curve in Fig. A3.1 with the dimensionless time, $Z^2 t/D_0$, as the ordinate and a dimensionless concentration,

$$\frac{Q_s \sqrt{D_0 a_c} C_{oi}}{T_{ikc} [1 + (k_g/k_c) \sqrt{a_c/a_g}] [(T_s/T_i) - 1]}$$

as the abscissa. The solid curve may be used to determine the effect of oxidizer concentration on ignition time when the concentration of oxidizer is varied by changing the mole fraction of oxidizer while holding the pressure constant (constant D_0)¹¹.

The other curved lines are plots of Eq. A3.24 when concentration changes are brought about by changing the total pressure while holding the mole fraction of oxidizer in the gas-phase constant. The broken curves thus make possible a direct comparison between the effect of changing the concentration by changing the mole fraction and the effect of changing the concentration by changing the pressure. The expressions for abscissa and ordinate for each dashed curve have the same functional form as those for the solid curve, but the true diffusion coefficient for each variable pressure (broken) curve is replaced by a reference value of the diffusion coefficient.

To amplify the method of obtaining the broken curves of Fig. A3.1, each computed point on a variable pressure curve was obtained by first assuming a reference value of the abscissa on the solid curve and determining the shift in coordinates on the solid curve which would result from a specified pressure change. In this calculation the diffusion coefficient was assumed to vary inversely with the pressure. These coordinates were then altered by replacing the diffusion coefficient with the value of the diffusion coefficient for the reference abscissa and adjusting the values of the new coordinates in such a manner that they could be plotted in Fig. A3.1 using the same functional forms for the dimensionless variables as were used for the solid curve. The broken curves thus provide a means for direct determination of any effect that the method of changing the oxidizer concentration may have on the ignition time predicted by the model.

Abscissa reference values of ten and two were used to compute the variable pressure curves. The reference value of the abscissa may be considered equivalent to fixing the mole fraction of oxidizer used in the calculation of the variable pressure curve. The dashed curve virtually coincides with the solid curve at high values of the abscissa, but breaks away considerably at the lower values of the abscissa. This behavior indicates that at the reference point the system was primarily controlled by kinetics; therefore, for larger values of the abscissa, the changes in the value of the actual diffusion coefficient were relatively unimportant. However, for values of the abscissa progressively lower than the reference value, the reaction becomes increasingly more affected by diffusion, and the variable pressure curve (which has the larger diffusion coefficient in this region) is relatively less affected by diffusion than the constant pressure curve and so diverges less from a slope of -2.

¹¹The solid curve also applies when the concentration of oxidizer is changed by varying the total pressure, but in this case D_0 as well as C_{O_i} becomes a function of pressure.

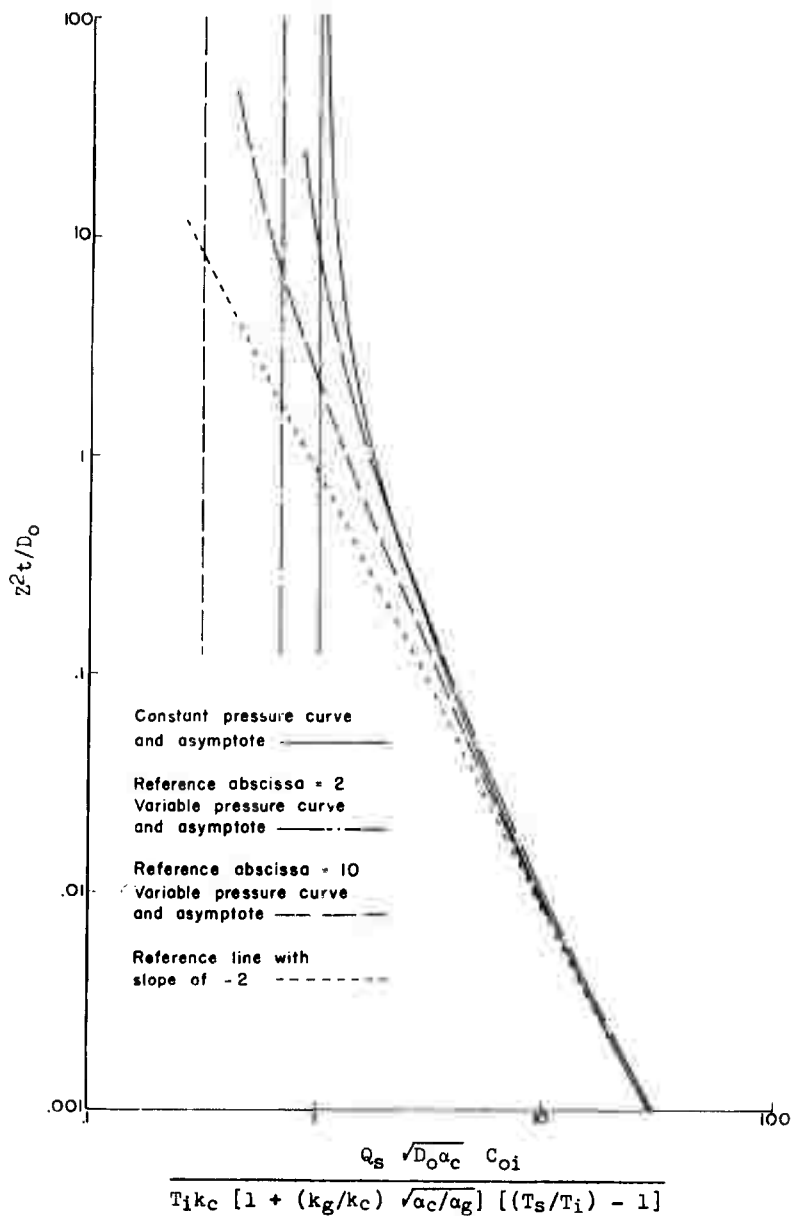


FIG. A3.1. Non-Dimensionalized Ignition Time as a Function of a Non-Dimensional Oxidizer Concentration (Assumed First Order Reaction and Zero Activation Energy).

In the case of the dashed and dotted curve, since the reference point was further into the diffusion controlled region, the curve to the left of the reference point was closer to the solid curve than in the previous example, because the relative change in the diffusion coefficient due to pressure change was less. On the other hand the curve is above the reference curve to the right of the reference point since in this region the diffusion is now still important, and as a consequence the reaction rate is slower for the variable pressure curve (lower diffusion coefficient). The dashed and dotted curve was computed for still smaller values than those shown in Fig. A3.1 and, when the abscissa was approximately 100, the dashed and dotted curve was virtually identical with the solid curve, indicating that once again the effect of diffusion on the reaction rate was negligible. The part of the curve or curves in Fig. A3.1 which are of interest will depend on the range of values of the parameters.

A3.3. COMPARISON BETWEEN SPECIAL MODELS AND THE GENERAL HYPERGOLIC MODEL

The agreement between the special models in this appendix and the results presented in Ref. 5 and 6 was investigated by comparing the trends shown in Fig. 3.3 through 3.7 with the behavior predicted by Eq. A3.2, A3.19, and A3.24. All of the models in the appendix assumed a constant surface ignition temperature; for purposes of this comparison a constant initial temperature will be assumed so that T_s^*/T_i becomes a constant. In all three analytical models the value of the temperature-time derivative at the surface was unsuitable as an ignition criterion. This result could be anticipated, since there was no temperature dependence in the reaction rate expression. In general one would expect the heat flux at the surface to be decreased with time because of the effect of diffusion, as was indicated to be the case for the third model, which allowed for both the effects of diffusion and kinetics. Equation A3.19 applies only to systems in which diffusion is unimportant. The other limitations on the models were discussed in the previous sections of the appendix and will not be listed here. However, when any additional restrictions to an equation are made, they will be pointed out in the discussion.

Fig. 3.3 predicts a slope of $-2a$ for a log - log plot of t^* vs. Co_i . The same slope is predicted by Eq. A3.19, and also by Eq. A3.2, if the groups involving D_0 are deleted (i.e., diffusion assumed unimportant).

Fig. 3.4 predicts a slight dependency of the slope on the activation energy, while Eq. A3.2 minus the diffusion groups shows no such effect. It should be pointed out that the curve for E equal to zero in Fig. 3.4 has a slope of precisely -2 , as was predicted for the kinetically controlled model. The parameters were adjusted in Ref. 5 and 6 so that the curves for different values of E would coincide at the point of highest concentration. At lower concentrations the time during which the surface

temperature would be relatively low is stretched out, and it would seem at least plausible that the ignition time for the cases of E not equal to zero would increase relatively more because of the lowering of the oxidizer concentration, than would be the case for the temperature independent kinetics (E equal to zero).

On the assumption that the arrow in Fig. 3.5, taken from Ref. 5, is reversed in sign, the effect of changing Z would agree qualitatively with the trend predicted by Eq. A3.2, A3.19, and A3.24.

Figure 3.6 from Ref. 6 indicates that t^* is approximately inversely proportional to $Q_S^{0.5}$, while Eq. A3.2 minus the diffusion terms and Eq. A3.19 indicate that t^* is inversely proportional to Q_S^2 when diffusion is unimportant. This contrast between results would imply that some effect of diffusion was present, and that the effect of w_S on the behavior of the ignition model is somewhat dependent on other parameters.

Figure 3.7 from Ref. 6 predicts that t^* is directly proportional to k_c , and, if heat transfer to the gas-phase and diffusion effects are considered negligible, Eq. A3.4 and Eq. A3.19 also predict that t^* is proportional to k_c .

In summary, the predictions based on the dimensional analysis and the analytical models appear to agree reasonably well with the results shown in Fig. 3.3 through 3.7. The results reported in this appendix show that the slope of $\log t^*$ vs. $\log C_{O_2}$ for the model is dependent on the concentration and parameters and can vary over a considerable range. The slope when the kinetics are fully controlling is $-2a$ and at the other extreme (diffusion limited) is infinite. The results of Ref. 5 and 6 seem to indicate that the reaction is predominately controlled by kinetics over the range of variables studied, and for this condition the effect of pressure is relatively small. The extent to which this generalization is relevant has not been fully assessed, but it is not likely to be applicable at very low oxidizer concentrations, or at pressures close to the low pressure deflagration limit of the propellant.

NOMENCLATURE

- A_1, A_2 Dimensionless groups
- a Reaction order
- B_1, B_2 Dimensionless groups
- B_c Coefficient of term for bulk chemical heating of solid ($=\rho_c Q_c Z_c$),
cal/cm³ sec
- B_s Coefficient of term for surface chemical heating, cal/cm² sec
- b_1, b_2 Coefficients in equation expressing ignition delay vs. temperature
- C Concentration
- c Specific heat at constant pressure, cal/gm^oK
- D Mass diffusivity, cm²/sec
- d Exponential decay constant for time dependent radiant flux, sec⁻¹
- E Activation energy, cal/mol
- f Fraction of reactant remaining unconsumed
- H Film coefficient for convective heating, cal/cm² sec^oK
- h Reduced film coefficient, $(-H/k)$, cm⁻¹
- h Dimensionless film coefficient used in Hicks's theory,
($= (E_c / R k_c B_c)^{1/2} H$)
- k Coefficient of thermal conductivity, cal/cm sec^oK
- M Molecular weight
- \dot{m} Mass flux, gm/cm² sec

- N_L Lewis number, ($= D/\alpha$)
- p Pressure, dynes/cm²
- Q Heat evolution accompanying a chemical or physical change, cal/gm
- q Energy per unit area from radiative, conductive, or convective sources, cal/cm² (used without subscript denotes radiant source)
- \dot{q} Energy flux per unit area, cal/cm² sec
- R Universal gas constant = 1.98 cal/mol^oK
- r Linear regression rate of solid surface, cm/sec
- T Temperature, ^oK
- T_{g1} Gas-phase temperature during high temperature heating pulse (Hicks's theory)
- T_{g2} Gas-phase temperature after high temperature heating pulse (Hicks's theory)
- ΔT_s Increase in surface temperature
- t Time, sec
- t_h Heating period in Hicks's theory
- v Chemical reaction rate
- x Space variable, cm
- Y Mol fraction
- Z Pre-exponential factor
- α Thermal diffusivity, cm²/sec
- β Extinction coefficient for radiant transmission, cm⁻¹
- δ Exponent in correlation of \dot{M}_{fsi} and p
- ζ Constant in expression for time dependent radiant flux
- n Dimensionless concentration

- θ Dimensionless temperature, RT/E
- v Fraction of exposed fuel surface
- ξ Dimensionless distance in gas-phase theory
- ρ Density, gm/cm^3
- σ Stoichiometric ratio
- τ Dimensionless time, defined by Eq. 4.14 in gas-phase theory
Dimensionless time in Hicks's solid-phase theory = $(B_c R / \rho_c c_c E_c) t$
- φ Factor defining ignition temperature
- χ Factor expressing effect of conductive heat loss from surface
- ψ Ratio of mass of product gases to mass of oxidizer reacted

SUBSCRIPTS

- a Adiabatic
- c Condensed phase
- f Fuel
- g Gas phase
- i Initial (zero time)
- k Conductive
- l Computed by neglecting chemical reaction
- m Fusion
- n Non-radiant
- o Oxidizer
- p Product
- s Surface ($x = 0$)
- ss Steady-state

SUBSCRIPTS (Contd.)

v Vaporization

∞ At a great distance from the surface

SUPERSCRIPT

* Ignition condition

NOTE: For simplicity in writing certain expressions, subscripts may be omitted when no confusion is likely to arise.

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<p>Surface ignition of solid propellants has been represented by several analytical models, each involving obvious compromises with regard to scope of applicability. These models are distinguishable primarily in terms of site of the exothermic reaction governing ignition. Early research with nitrocellulose led to development of a theory involving chemical heat generation in the condensed phase. Two subsequent theoretical models were developed to explain ignition of the solid fuel ingredient of a composite propellant in an oxidizing atmosphere, and these two models were then extended on a heuristic basis to encompass a composite propellant in an inert atmosphere in which the oxidizing gas was produced by decomposition of the solid oxidizer. These two models are distinguished by whether the oxidation occurs at the surface or in the gas film above the surface.</p> <p>This report reviews the solid, heterogeneous, and gas-phase ignition theories and reviews the nature and implications of the assumptions involved. It is concluded that, while possessing certain drastic simplifications in common, the various quantitative models differ so conspicuously in their assumptions regarding external initiating stimulus as to make quantitative comparisons or tests of validity impossible.</p>		

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There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.

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ABSTRACT CARD

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